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November 15, 2002

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the fourth-quarter FY 2002 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from http://berc.lbl.gov/BATT/BATT.html.

Sincerely,

Frank McLarnon

Frank McLarnon
Manager
BATT Program

cc:	R. Sutula	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	K. Abbott	DOE-Oakland

LBID-2445

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

QUARTERLY REPORT

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Task Status and Progress Toward Milestones Reports by Research Area

BATT TASK 1
CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to benchmark the performance of new materials for low-cost and high-power Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell, tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PIs involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, namely Li metal/polymer/V_6O_{13}, will be carried out in BATT Program Task 3.1.

STATUS OCT. 1, 2001:
- Cell fabrication and testing equipment, procedures, and protocols are in place for studies of 12 cm^2 laminated-foil pouch cells at various temperatures and constant-current cycling studies.
- Gen 2 chemistry pouch cells with both Quallion and LBNL-made cathodes were cycled 160 times with <5% capacity fade, providing verification of the pouch cell process.
- The high-power baseline cell chemistry has been benchmarked in constant-current testing. Cells have been received from Hydro-Québec for the benchmarking of the high-energy baseline cell against current USABC goals.

EXPECTED STATUS SEPT. 30, 2002: The effort on the low-cost Li-ion baseline cell will be focused on $LiFePO_4$ cathodes, various gel electrolyte components applied to Celgard, and the evaluation of the available natural graphites. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies. Studies of cell and component performance as functions of temperature and electrolyte composition will be completed. Evaluation of new materials for the baseline cells will be underway: $Li_{0.44}MnO_2$ (LBNL), $LiMn_{2-y}Al_yO_{4-z}S_z$ (LBNL), intermetallic anodes (ANL), and layered Mn-based cathodes (ANL).

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period.

MILESTONE: (a) Evaluate cycle-life and power capability of the $LiFePO_4$/gel with $LiBF_4$/natural graphite cell (December 2001). (b) Compare the several approaches to gel-electrolyte cell assembly using standard Li-ion electrodes (June 2002).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:**

Work this quarter has continued to focus on the low-cost baseline cell with a $LiFePO_4$ cathode and a natural graphite anode. A new batch of $LiFePO_4$/gel/natural graphite cells was received from Hydro Quebec. This batch contained their gel electrolyte with either pure $LiBF_4$ or a mixture of $LiBF_4$ and LiTFSI electrolytes with EC/γBL as the solvent. Testing of the batch of ten cells has been completed, including calendar and cycle life studies. Preliminary analysis of the results shows that this batch demonstrated the best performance yet for the low-cost baseline cell with gel electrolyte. The benchmarking numbers of 0.53 mAh/cm^2 for the specific capacity and a specific energy of 1.7 mWh/cm^2 were recorded at the C/3 rate. This is about 28% higher than the previous batch. The improvement is due to an increase in cell stability both with calendar and cycle life. However, the capacity still fades at an unacceptably high rate. Electrode samples from this batch will be delivered to the diagnostics tasks to help identify the source of the capacity fade. Results to date point to a mechanism where the cycleable lithium is being consumed.

In order to further understand the nature of the rapid capacity fade observed with our 12-cm^2 $LiFePO_4$/liquid/natural graphite pouch cells, several cells were assembled and tested with different electrolytes, anode active materials and cell designs. Half-cell studies of the $LiFePO_4$ cathodes and graphite anodes suggest that all of the electrodes show very stable cycle behavior against a Li metal counter electrode. However, when assembled in a full cell configuration with either $LiPF_6$ or $LiBF_4$ electrolyte, the capacity at C/2 cycling fades at unacceptably high rates. Swagelok full cell studies, with high compression of the cell pack, showed better rate capability but similar fade rates. The $LiPF_6$ electrolytes showed better rate capability as well, due to the higher conductivity of this electrolyte. Electrochemical diagnostics show that in all cases so far, the primary reason for capacity fade is the consumption of cycleable Li. The electrode samples removed from cycled cells demonstrate performance essentially the same as a fresh electrode when paired with a Li metal counter electrode.

Studies of the effect of anode compression on anode resistivity, performance and cycle life has been initiated out with the SL-20 natural graphite from Superior graphite, and two Mitsui Mining natural graphites with 6 and 14wt% coating of amorphous carbon. This is being done in collaboration with U. Michigan. One-cm^2 electrodes with coating densities in the range of 0.6 to 1.9 g/cc are formed against Li in a Swagelok cell with LP40 electrolyte and then cycled at C/2. Preliminary results show that matrix conductivity increases and order of magnitude with a doubling of the anode density for all three carbons. The amorphous-carbon coating greatly improves conductivity and contact resistance with the current collector compared to the SL-20. Increases in anode density improve the efficiency of the Mitsui carbons but has only minimal effect on the efficiency of the SL20. However, the first-cycle efficiency of the Mitsui carbons is lower than the SL20 in proportion to the amount of the amorphous coating. Studies of the relative stability of these anode materials during cycling will be reported next quarter.

Gel electrolyte cells were assembled with five types of gel electrolyte and high-energy $LiCoO_2$ and graphite electrodes from Quallion. The gel samples from Daiso showed promising performance in one cell, but the result was found to be very difficult to reproduce. A decision was made to pursue the PVdF type gel electrolyte cells because of greater ease in cell assembly.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: *Subtask 1.* Address primary causes of capacity and power fading by correlating them with the composition and structure of electrode active materials using x-ray diffraction (XRD), vibrational spectroscopy, and voltammetry. *Subtask 2.* Develop internal overcharge protection mechanism that becomes active when needed and allows continued, undegraded cycling of unaffected cells. *Subtask 3.* Develop improved cathode materials *via* a rational approach to active material synthesis.

STATUS OCT. 1, 2001: The stability of $LiFePO_4$ at extreme potentials and states of charge has been established. Capacity fading in $LiFePO_4$ due to overcharging has been shown to be due to loss of active material rather than to phase conversion. New phosphate-stabilized cathode materials with high Li content were prepared and characterized.

EXPECTED STATUS SEPT. 30, 2002: Phase transformations and accumulation of decomposition products in cycled electrodes from Task 1.1 will be identified and correlated with cell performance characteristics. The ability of electroactive polymers to provide overcharge protection will be evaluated. Potentially useful new low-cost, high-capacity electrode materials will be synthesized and tested.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Determine phase transformations in cycled cathode materials selected for use in BATT Cell development tasks (April 2002). Determine switching characteristics of electroactive conducting polymer (June 2002). Prepare and characterize novel stabilized Fe and/or Mn cathode materials (August 2002).

PROGRESS TOWARD MILESTONES

Milestone 1. Developed new analytical methods and determined phase transformations in cycled cathode materials ($LiFePO_4$, ATD Gen-2) as reported previously. *Status: Achieved.*

Milestone 2. A method was developed for uniform electrochemical deposition of conducting polymer on Celgard membrane under the Li battery cell conditions. By solution coating one side of the membrane with conducting polymer prior to electrodeposition, better electric contact of the membrane with the current collector was achieved during polymerization in the monomer solution. This led to polymer growth on the entire surface area rather than around the edges as observed when using untreated membranes. The process is promising for use as overcharge protection through an internal short mechanism in the cell. Conducting polymer was also prepared on stainless steel mesh and ITO glass. In the latter case, the deposited polymer formed a continuous film, which can easily be peeled off from the glass substrate as a freestanding film, in either oxidized or neutral form.

Commercial conducting polymers are available in either a neutral, insulating form (alkyl substituted polythiophene series) or an anion-doped, conducting form (polypyrrole, polyethylenedioxythiophene). The doped polymers are usually sold in aqueous solution, and they tend to peel off from the substrate when the solvent is fully removed. Our early efforts toward making neutral polymer films involved spin coating or casting of polymer solutions (typically using CHCl3). Although uniform films were obtained, when the films were electrochemically oxidized, anion intercalation altered the structure of the polymer and eventually destroyed its integrity. To solve this problem, a less volatile solvent, DMF, was added prior to casting. This produced polymer films with higher porosity, roughness, and flexibility. CV studies showed that such prepared films were preserved intact during the oxidation process.

The relationship between SOC, conductivity and OCV of a conducting polymer is important in understanding its characteristics as a charge carrier, and these data are essential inputs for the model of the system being developed by Karen Thomas. An electrode was designed to allow adjusting the oxidation state of the polymer electrochemically, while sequentially measuring its conductivity. A neutral polymer film is cast on a piece of stainless steel plate. A second stainless steel plate provides contact for the conductivity measurements. The polymer is brought to the desired SOC and its OCV is recorded after relaxation. The electronic conductivity of the polymer is measured by AC impedance. The conductivity of the polymer increases with OCV and SOC. In poly (3-butylthiophene), a conductivity increase of 4 orders of magnitude was achieved by charging in a battery electrolyte to an SOC of about 50% (Fig. 1). Further charging is expected to give much higher conductivity. *Status: In Progress. Completion expected by December 2002.*

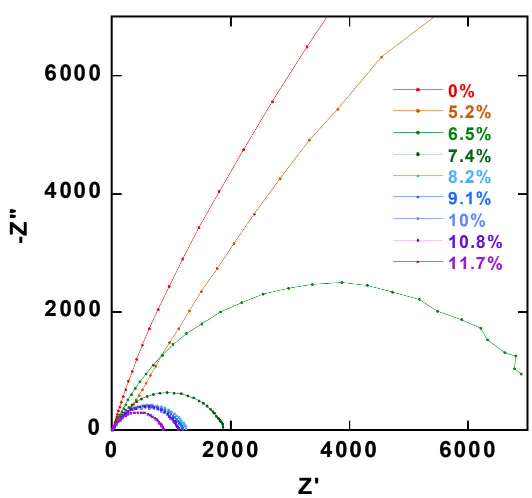


Figure 1. Impedance plots for poly (3-butylthiophene)$^{+}PF_6^{-}$ at various states of charge.

Milestone 3. New manganese and iron phosphates with stoichiometries similar to that of $Li(Fe,Mn)PO_4$ but with better electronic conductivity, intercalant ion mobility, and ease of preparation were prepared and tested in Li cells. Their reversible capacities were found to be unacceptably small. *Status: Achieved.*

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec Research Institute

TASK TITLE - PROJECT: Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: (a) To fabricate Li-ion polymer cells (4 cm^2 area) using cell chemistries proposed by DOE. Cells (50% of total) will be sent to LBNL for testing. (b) To investigate phenomena at the anode/separator and cathode/separator interfaces. (c) To determine the cycle life of Li-ion polymer cells at different temperatures (55 to 0°C) and self-discharge rates. (d) To synthesize $LiFePO_4$ cathode material for Li-ion polymer cells.
We want to determine the effects of: (1) $LiFePO_4$ particle size, (2) the amount of conductive carbon in the electrodes, (3) the mixed salt concentration (from 1 M to 2 M), on battery performance.

APPROACH: Our approach is to synthesize and prepare electrodes (anode and cathode) with low-cost materials for evaluation in Li-ion polymer cells containing gel polymer electrolytes. The effects of $LiFePO_4$ particle size, the amount of conductive carbon in the electrodes, and the salt concentration (mixed salt, from 1M to 2M) on battery performance will be investigated. The effect of pressure and interfacial phenomena on electrode performance will also be studied.

STATUS OCT. 1, 2001: We completed the coating of electrodes containing graphite, $LiFePO_4$ and $Li_4Ti_5O_{12}$ with variable capacities. Samples of these coated films were sent to LBNL for evaluation. Li-ion gel polymer cells were fabricated and testing was underway.

EXPECTED STATUS SEPT. 30, 2002: Complete tests and validation on the mixed salt. Complete in-situ SEM characterization on gel Li-ion cells cycled at 0°C. Identify the optimal $LiFePO_4$/carbon composition for evaluation in Li-ion gel cells.

RELEVANT USABC GOALS: 10 year life, < 20% capacity fade over a 10-year period.

MILESTONES: Ten cells were provided to LBNL in July 2002 for evaluation. A second batch of ten cells based on the chemistry graphite/gel polymer/$LiFePO_4$ will be sent to LBNL in November 2002. $LiFePO_4$ powders of different particle size and coated films containing these particles will be sent to LBNL. The cell assembly using all gel type cells (anode, cathode and electrolyte) by in-situ cross linking will be optimized.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We studied the effect of solvent mixture and lithium salt on the performance of Li-ion polymer cells. HQ solvent (TESA) mixed with EC (3/1) was found comparable to GBL-EC (3/1) in electrochemical performance. For the mixed salt (1MLiTFSI + 0.5$LiBF_4$ in EC/GBL) higher capacity fade (Fig. 1) compared to the same molar concentration of single salt (LiTFSI or $LiBF_4$) was observed. We are analyzing this phenomena in half cells with Li/graphite and Li/$LiFePO_4$.

We completed coating of $LiFePO_4$ electrodes with different amounts of conductive carbon (1% to 15%). In electrodes with 9% and 12% conductive carbon, we used a mixture of carbon black and graphite (3%, 6%) and (6%, 6%), respectively. The aim of these experiments is to identify the optimal cathode composition to improve high-rate performance. The data in Figure 2 show that increasing the carbon content in the iron phosphate cathode has a dramatic effect on high-rate performance. A 6% carbon content seems to be a good compromise with energy and power, with 65% of the reversible capacity at 2C-rate and 62% at 3C-rate. Even with 1% carbon, we obtain more that 50% of the reversible capacity at 3C-rate.

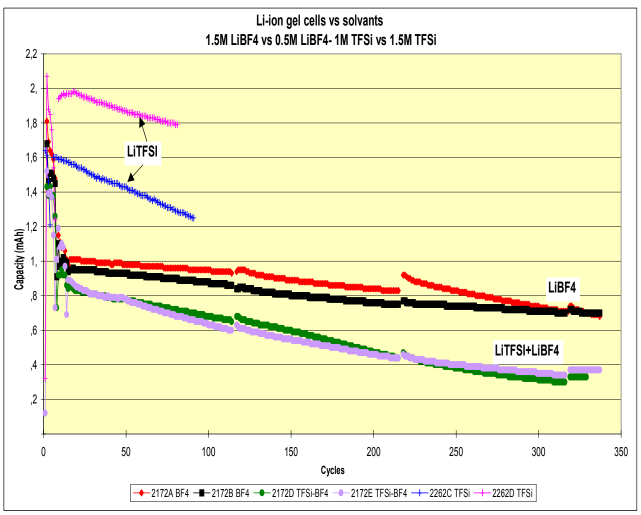


Figure 1

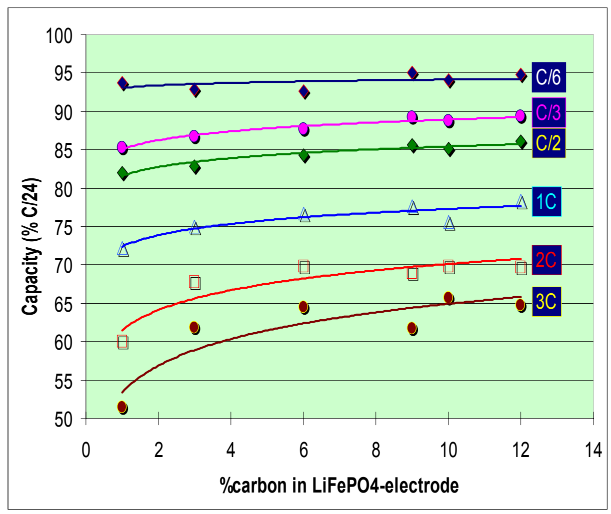


Figure 2

Recently, our effort focussed on in-situ SEM studies of gel polymer cells at 0°C. The cells were cycled under vacuum in the electron microscope using electrolyte based on GBL which has high boiling point.

Ten (10) cells with different salt EC/γ- GBL (1:3) were delivered to LBNL in July 2002.

- **Further plans to meet or exceed milestones:** We plan to develop thermal cross-link gel polymers by using IR technology. This technology will help reduce the cost of Li-ion gel cells.

- **Reason for changes from original milestones:** N/A

BATT TASK 2
ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2001: We identified intermetallic compounds with various structure types that convert to lithiated zinc-blende-type structures during reversible electrochemical reactions. Cu_6Sn_5, InSb, and Cu_2Sb have formed the basis for our studies. Cu_2Sb yielded the best electrochemical performance and stability. Against a Li electrode, Cu_2Sb delivered a stable capacity of ~300 mAh/g, which translates to 1914 mAh/ml, for at least 25 cycles. These novel intermetallic electrodes, which operate by a reversible Li insertion/metal extrusion reaction with an invariant metal host subarray, provided a new approach for the design of alternative anode materials with acceptable capacity, performance, and stability.

EXPECTED STATUS SEPT. 30, 2002: We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g and 2000 mAh/ml in Li half-cells (K. Striebel). Through collaborative efforts, we will have studied the nature of the electrode/electrolyte interface and obtained data on the thermal stability of the intermetallic electrodes with respect to the electrolytes. Detailed structure/electrochemical property relationships will have been obtained primarily by XANES, EXAFS, and XRD studies at the Advanced Photon Source at Argonne and by HRTEM imaging.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: Our primary milestone will be to achieve a reversible electrochemical capacity of tin and/or antimony based intermetallic electrodes in excess of 300 mAh/g and 2000 mAh/ml for more than 100 cycles by April 2002. Efforts to understand structure/electrochemical property relationships, electrode/electrolyte interfaces, and thermal stability of the intermetallic electrodes will be on going through September 2002.

PROGRESS TOWARD MILESTONES

• **Accomplishments toward milestone over last quarter:** During FY2002, it was established that the major performance limitation of intermetallic electrodes that had been identified at ANL was the irreversible capacity loss that was observed during the initial charge and discharge cycle. Moreover, this limitation has compromised our ability to achieve the targeted reversible capacity of the electrodes (300 mAh/g). However, our recent studies of MnSb electrodes have demonstrated that, after the initial cycle in which the capacity loss was sometimes less than 20%, a capacity exceeding 300 mAh/g can be obtained for the first 20 cycles when Li/MnSb cells were charged and discharged between either 1.5 or 1.2 and 0 V (Fig. 1). However, on continued cycling, the capacity fell below 300 mAh/g. The reaction, which involves a structural transformation of MnSb to Li_3Sb via an intermediate LiMnSb phase, was shown by in-situ X-ray diffraction to be highly reversible at room temperature, but with some hysteresis that was associated with the diffusion of the Sb atoms during the transformation of MnSb to LiMnSb (Fig. 2).

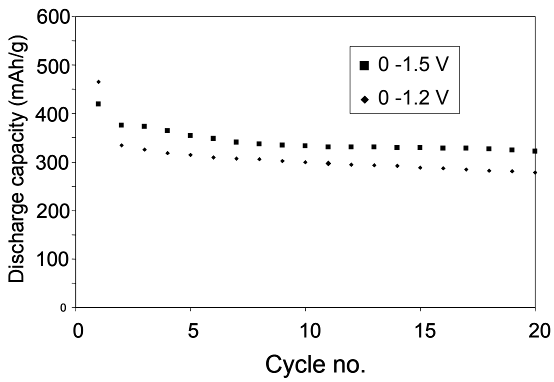


Figure 1. Capacity vs. cycle no. for a Li/MnSb cell.

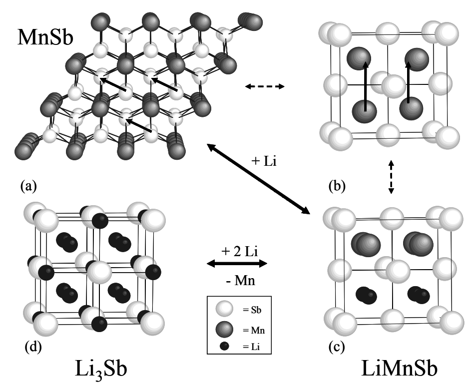


Figure 2. The reversible structural transformations that occur between MnSb and Li_3Sb.

Efforts were launched to find ways to counter the initial capacity loss by including Li in the intermetallic electrode during cell assembly, either as a Li salt or as a component of the intermetallic structure. For example, a Cu_2Sb electrode was ball milled with 5% by weight of lithium carbonate, lithium fluoride, or lithium hydroxide; the X-ray patterns of the ball-milled samples showed the expected mixtures of compounds. However, these composite electrodes showed no electrochemical advantage. We are now currently investigating the possibility of incorporating the Li within intermetallic structures such as $Cu_{6-x}Li_xSn_5$ and $Cu_{2-x}Li_xSb$ in which some solid solubility between Cu and Li in the structure can be expected.

Further plans to meet or exceed milestones: During FY2003, we will continue efforts to meet our performance goal for intermetallic electrodes: 300 mAh/g for 100 cycles. We intend to study the thermal and safety properties of intermetallic anode systems by DSC, ARC and microcalorimetry, and to expand our efforts to include Si-based systems. We will also explore the possibility of using electronically-modified $Li_4Ti_5O_{12}$ anodes against 5 V cathode materials.

Reason for changes from original milestones: A study of thermal properties is required in order to determine what safety advantages lithiated intermetallic electrodes have over lithiated graphite. The discovery of 5 V electrode materials that are structurally stable to lithium insertion/extraction, offers the possibility of designing safe 3.5-3.0 V lithium-ion cells with $Li_4Ti_5O_{12}$-type anodes.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular we will investigate Mn-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2001: We determined that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al was found to have a high capacity and it reacted readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes. Several simple binary alloys of Al showed an even higher capacity fade than Al itself. Tin-containing materials, such as $MnSn_2$ appeared to cycle well for a few cycles, before capacity fade set in.

EXPECTED STATUS SEPT. 30, 2002: We expect to identify several additional non-Al binary alloys, to improve the electrochemical performance of the materials identified, and to design a program to understand and remediate capacity fade upon cycling.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify by September 2002 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 volts relative to pure Li. In addition, we will design a program to identify, understand and mitigate the capacity loss during cycling of simple alloy systems.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

As agreed in the AOP we are now generating a plan to build a better understanding of the capacity loss in simple binary metal systems, particularly for carbonate based electrolyte systems. One example is $MnSn_2$, which cycles well for a few cycles then decays rapidly. There is a complete reaction (turnover) of the tin of around five before degradation sets-in indicating that the compound is inherently reversible. We will compare this system with the SnBi eutectic, where Sn and Bi are present as separate species and no compound formation occurs on lithium removal.

We have placed major emphasis in the last quarter in understanding the behavior of pure tin as an anode material. This will then be a reference for all other tin-containing anode compositions. In order not to have any complications from secondary phases, tin foil was chosen as it can be used without the addition of any conductive diluent like carbon or of a binder. Surprisingly, there is very little published data on pure tin; most of the data is on tin powders of varying particle size admixed with conductors and binders.

Commercial tin foil was rolled and then used as-is as the electrode in a carbonate based electrolyte cell with a pure lithium counter-electrode. The cycling capacity is shown in Fig. 1 (left), and as can be seen the capacity is essentially maintained for more than ten cycles before a marked fall-off is observed. The maximum capacity observed is around 3.6 Li/Sn rather than the expected $Li_{4.4}Sn$.

In an attempt to determine what might be causing the capacity fall-off, an impedance study was carried out on almost completely discharged tin electrodes as a function of number of cycles completed. The preliminary results are shown below. It can be seen that the cell impedance increases at the same time as the cell capacity decreases. There is clearly a correlation here, and we are now determining the source of this impedance increase and why it should suddenly increase around ten cycles.

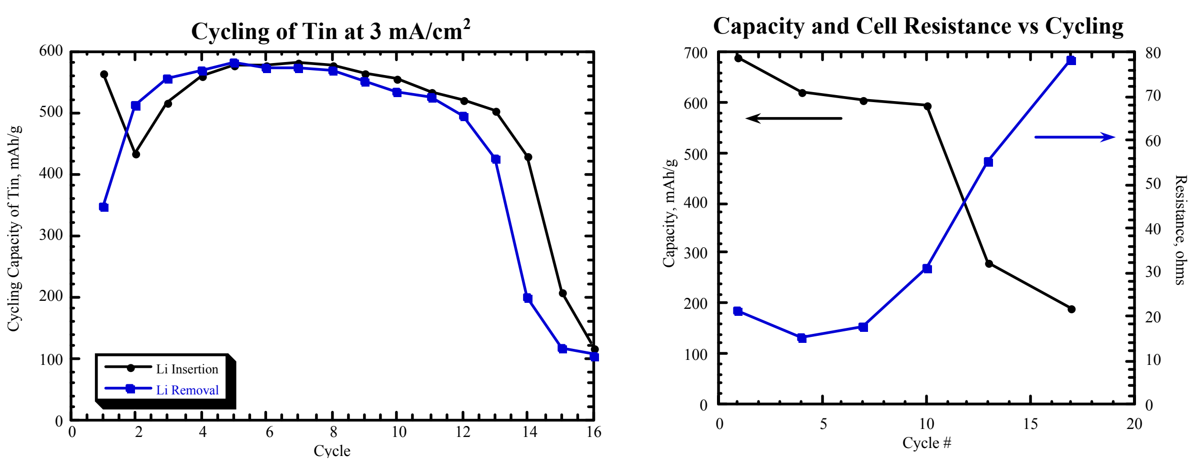


Figure 1. Capacity of tin foil on continuous cycling (left), and (right) resistance change and capacity change on a discharged cell after 5 hours rest as a function of cycle life.

- **Further plans to meet or exceed milestones:** None.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low–cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery through the development of a novel composite anode with no irreversible capacity loss during initial cycles, and with high energy and power density.

APPROACH: Our approach is to develop composite anode through prelithiation to remove the irreversible capacity loss and provide high performance anode with thermal and chemical stability for application in large size Li batteries. The composite anode will be engineered to be compatible with the existing Li-ion chemistry. The composite anode also provides a new opportunity to construct Li cells using lower cost and stable electrolytes.

STATUS OCT. 1, 2001: We have proposed to develop a composite anode with no irreversible capacity loss and with superior gravimetric and volumetric energy density. Further, this new composite anode will provide a new opportunity to be used in combination with high energy and high rate non-lithiated cathodes that will allow the use of much lower cost electrolytes (PC-based electrolytes). While the focus of our work will be on the development of composite anode, during 2001, we have also developed a Li-phosphonate polymer that is stable in the operational voltage range of carbonaceous anodes with the added benefit of expected fire retardant properties. Also, a unique, *in situ* technique was developed for exploring the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2002: A novel composite anode with no irreversible capacity loss will be delivered for application in large size Li-ion batteries. The main focus will be on optimization of rate capability, energy density, and safety aspects of the composite anode. The novel process to be developed in this work is applicable to alternative anodes such as carbonaceous anodes, oxides, nitrides, and phosphides systems. Further, the electrode impedance will be minimized for application in high-power batteries.

RELEVANT USABC GOALS: Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries, and new opportunity to develop practical battery for HEVs and EVs.

MILESTONES: (a) Synthesize a new composite anode with no irreversible capacity loss and with superior energy and power density as compared with those of the current carbonaceous anodes. (b) Develop a low cost chemical process to remove irreversible capacity loss form composite anodes for lithium-ion technology.

PROGRESS TOWARD MILESTONES

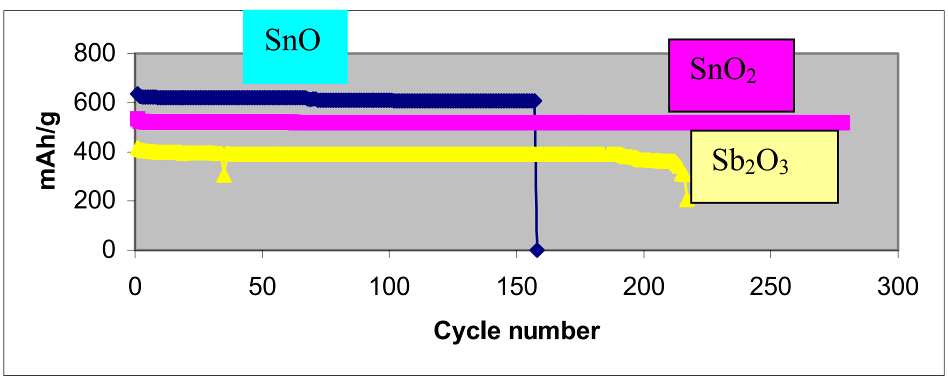
- **Accomplishments toward milestone over last quarter**

The work has been focused on the development of a safe composite anode with higher energy density and power rate capability than the current carbonaceous and graphitic anodes. The synthesis of the new composite anode involves the mechanomilling process of the oxides and nitrides with lithium containing precursors according to the following equations:

$$MO_x + 2xLi \xrightarrow{\text{Mechanomilling}} [xLi_2O + M]_{composite} \underset{y(-Li^+ - e^-)_{discharge}}{\overset{y(+Li^+ + e^-)_{charge}}{\rightleftarrows}} (Li_yM)_{active\ phase}$$

$$MN + 3Li \xrightarrow{\text{Mechanomillin}} [Li_3N + M]_{composite} \underset{Y(-Li^+ -e^-)_{discharge}}{\overset{Y(+Li^+ + e^-)_{charge}}{\rightleftarrows}} (Li_yM)_{active\ phase}$$

The large irreversible capacity loss of oxides and nitrides are eliminated by mechanomilling process with Li containing precursors. The nano-scaled metal phase is formed during milling process is protected by the ionic coating and serve as an active anode phase during charge and discharge of the Li cell. We have studied several oxides and nitrides using the mechanomilling process. Anode plates were made and tested in conventional multi-blend carbonate based electrolyte, (EC-DMC-PC, 50:30:20, containing 0.8M $LiPF_6$). Results of electrochemical charge discharge cycles are shown. The best result in terms of charge-discharge cycles were observed for oxides with higher oxygen content; $SnO_2 > Sb_2O_3 > Sn_3N_4 > SnO$. The results indicate that the lithium oxide coating provides a more protective film than the lithium nitride films.



- **Further plans to meet or exceed milestones:** Our future plan is to optimize the prelithiation process in presence of electrolyte. In addition we will study the mixed oxide phases to form composite alloys. The scale-up of the prelithiation process using mechanomilling method is also in progress.

- **Reason for changes from original milestones:** N/A

BATT TASK 3
ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N. Balsara, J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4-V.

OBJECTIVES:
- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2001: A study of the effects of polymer electrolyte properties on dendrite growth at Li metal electrodes was completed. Polymer electrolytes were prepared that are designed to define the upper limits of ion transport for polymer electrolytes (conductivity $>10^{-4}$S/cm, $D_s>10^{-8}cm^2s^{-1}$ and $t^0_+>0.3$ at 20°C with LiTFSI). An initial survey of the effect of polymer structure on stability toward high voltage was initiated. Lab cell ($1cm^2$) testing of the Li/polymer system was established and baseline data sets completed.

EXPECTED STATUS SEPT. 30, 2002: Quantitative measurements of the primary factors involved in dendrite growth will be completed (transport and mechanical properties). Transport and mechanical properties will be measured for less costly salts (LiTf, $LiPF_6$ and $LiBF_4$) and the cost *vs.* performance will be assessed. Lithium/polymer and gel-polymer cell testing at an appropriate larger cell size (*e.g.*, 25 or $100cm^2$ area) will be established and compared with Lab cell performance. Diagnostics will be developed to characterize electrolyte/binder changes that cause increase of ASI and capacity fade.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment –40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150$/kWh @ 20K/year.

MILESTONES:
1. Electrolyte properties that inhibit dendrites measured quantitatively (09/30/02)
2. Complete scale-up for Li/polymer and gel polymer cell construction and testing (12/31/ 02).
3. Establish correlations between large scale and lab cell performance (09/30/02).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

1. Polymer Electrolyte properties that affect the growth of dendrites on lithium metal electrodes have been identified and measured. The effect of some of these properties is dependent upon the cell geometry. For this report a separator membrane thickness of 50 µm is assumed and a cathode thickness of 90 µm with a porosity of 60% is assumed. The following are the minimum values that are required to inhibit dendrite formation with a current density of 200µA/cm^2 for a total of 8,000 coulombs/cm^2 (1000 cycles, USABC goal):

- Transport Properties:
  - Conductivity - 5 x 10^{-4}S/cm
  - Salt Diffusion Coefficient – 4 x 10^{-8} cm^2/s
  - Transference number $t^0_+ > 0.3$
- Mechanical Properties :
  - Shear Modulus > 6 Mpa
  - Young's Modulus > 20 MPa
  - T_g polymer < -70^0C ; T_g polymer electrolyte (3 molar Li salt) < -60°C
  - Single T_g in dynamic mechanical analysis for uniformity of cross-linking.
  - Morphology profile variations in AFM after cross-linking < 10 nm.
- Impurities/additives :
  - Up to 10% nano-particulate desiccant such as fumed silica improves performance without severely affecting transport. Combination of fillers plus cross-linking chemistry allows gives the mechanical moduli listed above.
  - Up to 1000ppm H_2O or OH-containing compound (e.g., BHT) may be present.

These values change as the cell geometry changes. *This milestone is completed.*

3. Pouch cells (12cm^2) and Swagelok cells (3.14 cm^2) have been built and cycled with Li/V_6O_{13} electrodes and the smaller cells have been cycled with Li/Li half cells, Li/$FePO_4$ and Li/$LiMnO_x$ electrodes. Polymer electrolytes used with these cells include PEO with filler reinforcement, cross-linkable PEO, cross-linked polyacrylate ethers and polyepoxide ethers. Cross-linked PPO polymers have been provided to the Cell development Task for use as Gel Polymers that eliminate the use of Celgard and all of the above-listed materials are available in membrane form for incorporation as gels in pouch cell testing. The tests conducted so far with the larger pouch cells show good impedance behavior and good discharge characteristics. Charging appears to be affected more by dendrite growth which may be related to membrane creep. This problem will be solved by improvements in the large area membrane curing procedures to provide more uniform properties. The scale-up from 1 to 3.14 to 12 cm^2 cell area appears to be adequate for testing uniformity and to provide sufficient material for diagnostic testing. *This milestone is completed.*

Further plans to meet or exceed milestones. Experiments with addition of nano-particulate filler materials to polymer electrolytes show that the reported improvements are due to entrainment of water or other impurities. Careful experiments that exclude atmospheric exposure show that the fillers decrease the transport properties (conductivity and salt diffusion coefficient) while increasing the moduli. It is also noted that complete exclusion of atmospheric contaminants leads to capacity fade in full cell cycling. Apparently small amounts of H_2O, CO_2 and $O_2$and N_2 may be beneficial for the formation of surface films on either electrode that improves the cycling performance. These effects are under active study.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2001: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25ºC and have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^5 Pa). We determined that fumed silica stabilizes the Li/electrolyte interface effectively suppresses Li dendrite growth, and significantly improves cycle performance and electrochemical efficiency. We also observed that different surface groups present on the silica effect varied improvement on electrochemical performance in both half- and full-cell studies with a V_6O_{13} cathode. Fumed silica A200 having 100% hydrophilic silanol surface groups exhibits better electrochemical performance than R805 having 48% hydrophobic octyl surface groups.

EXPECTED STATUS SEPT. 30, 2002: Using the baseline high-molecular weight PEO + LiTFSI system, we expect to determine the effect of fumed silica on conductivity and electrolyte/Li interfacial stability and how these results vary with type of fumed silica surface group.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Develop protocols for incorporating varying amount of fumed silica with a variety of surface chemistries (*e.g.*, -OH, octyl-, and crosslinkable moieties) into LBNL baseline polymer electrolytes. (March 2002)
2. Complete Li/CPE/Li and full-cell cycling studies using 3-V vanadium oxide cathodes with composites developed from milestone 1. (September 2002)
3. Acquire rheological data for materials generated from milestone 1 for correlation with electrochemical stability. (September 2002)

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

We are using X-ray diffraction (XRD) and differential scanning calorimetry (DSC) to characterize base-line materials: high-MW PEO (6×10^5) + LiTFSI + fumed silica systems. In $P(EO)_{10}LiTFSI$ (O:Li=10) electrolyte, there are no X-ray diffraction peaks and no melting peak detected in the DSC data, both with and without fumed silica. At a salt concentration one-half of that above, $(PEO)_{20}LiTFSI$, there are two peaks at about 19° and 23° in the diffraction patterns. The peak intensity at about 19° decreases with addition of hydrophilic A200 or hydrophobic R805 fumed silica. There is a melting peak in the DSC data, with the on-set of melting at about 30°C and the peak temperature at about 50°C. There is also a glass transition at about -50°C. The on-set melting point, heat of melting, and glass transition temperature decrease with addition of hydrophilic A200 or hydrophobic R805 fumed silica. The degree of crystallinity of $(PEO)_{20}LiTFSI$ + 10% F.S. is 80% of the degree of crystalline of $(PEO)_{20}LiTFSI$, as determined both by XRD and DSC data. These results taken together indicate that fumed silica addition increase the conductivity through a decrease in crystallinity.

We have demonstrated with preliminary full-cell cycling of Li/electrolyte/V_6O_{13} cells that adding fumed silica improves the interfacial stability of lithium/composite polymer electrolyte $P(EO)_{20}LiTFSI$ (MW= 6×10^5). The vanadium oxide cathodes consist of 45 wt% V_6O_{13} (Kerr-McGee), 2.5 wt% graphite (Timcal American), 2.5 wt% Ketjen-Black600 (Akzo Nobel), and 50 wt% $(PEO)_{20}LiTFSI$ (MW=6×10^5). Aluminum foil is used as current collector. In the full-cell Li/electrolyte/V_6O_{13} system, cycle performance improves with addition of fumed silica when cycling at 0.08 mA/cm^2 from 1.8 to 3.0 V at 95°C. Further investigations and optimizing the composition of vanadium oxide cathodes continue.

We have measured the dynamic rheology at 80°C of high-molecular weight (MW=6×10^5) PEO samples containing 0 and 10 wt% A200 or R805. At this temperature, the neat PEO behaves like a classic viscoelastic polymer: viscous behavior at low frequency and elastic behavior at high frequency. A plot of the elastic modulus G' and viscous modulus G'' versus frequency crossover at 10 rad/s. The addition of fumed silica increases the elastic modulus and decreases the crossover frequency. At 10 wt% fumed silica, the crossover frequency is no longer observed in the measured frequency range (0.01 rad/s to 100 rad/s). This implies that the crossover frequency is less than 0.01 rad/s, which corresponds to a significantly long relaxation time and the onset of gel-like behavior. Thus, the fumed silica forms a network structure and provides mechanical support even when the PEO matrix has melted. The surface chemistry of the fumed silica affects the mechanical properties of the PEO as well: 10% A200 > 10% R805 > No F.S..

We also have begun to investigate baseline mixed-PEO system (i.e., low + high-MW PEO). Fumed silica in PEO mixtures electrolyte exhibits elastic-like properties.

Further plans to meet or exceed milestone: We continue to optimize the composition of vanadium oxide cathodes and study the full–cell cycling using Li/CPE/V_6O_{13}. We will continue to investigate PEO mixtures electrolyte.

•**Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Short Li battery lifetime. Low Li battery power density.

OBJECTIVES: (1) Develop methods for synthesizing oligomeric ionene Li salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on the ionic conductivity and Li transference of the target SPEs at variable temperature and composition. We expect these studies will lend insight into the effects of anion size, chain length, and linker structure on SPE ionic conductivity and Li transference.

APPROACH: Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem*. 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Conductivities will be measured using electrochemical impedance spectroscopy.

STATUS OCT. 1, 2001: Contract was signed to initiate project in late Jan. 2002.

EXPECTED STATUS SEPT. 30, 2002: Dimeric salts with different perfluorinated chains linking sulfonyl imide anion groups together, and oligomeric ionene salts utilizing the same linkers in longer chains, will have been synthesized. SPEs from the salts will have been fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions. A method for measuring Li^+ transference based on DC potentiostatic polarization is being implemented, and progress in measuring Li^+ transference in the target SPEs will have been made.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over 10 year period, 1000 cycles.

MILESTONE: Our two major project milestones are as follows:
1. Synthesize new ionene Li salts based on oligomeric bis((perfluoroalkyl)sulfonyl)imide anion structures.
2. Characterize the electrical properties of polyether-based solid polymer electrolytes from the target salts at variable temperature and salt content.

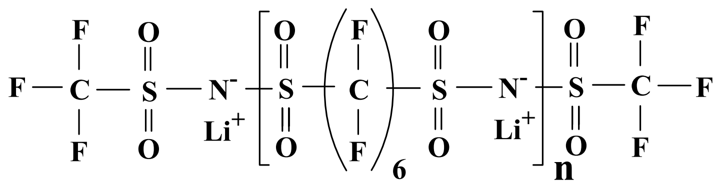
Progress toward the milestones will be ongoing as new salts are synthesized and are made available for characterization. Synthetic and characterization work on dimeric Li salts should be completed by Sept 30, 2002. Synthesis and characterization of oligomeric salts should be started and preliminary results obtained by Sept 30, 2002.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

Progress toward milestones from Jan 2002 - Sept 30 2002.. Synthesis of a series of dimeric Li salts with various fluorinated linker chains between two sulfonimide anions has been completed, and measurement of ionic conductivity and thermal properties (glass transition, PEO melting) of SPE's comprising these salts in a PEO matrix with and without use of tris-isocyanate crosslinking agents has been completed. Work aimed at evaluating Li transference in these SPEs is taking longer than anticipated due to a need to change methodology to a method that is more reliable but new to our group. Contact has been established with the group of Greenbaum at CUNY to use NMR techniques to measure Li and also anion (fluorine) self-diffusion rates in SPEs. These rates are needed to provide reliable parameters for making a restricted-diffusion measurement of salt diffusion, which will be made at Clemson. When this measurement is made we will collaborate with Doeff and Kerr at LBNL to make measurements of cell potential vs salt concentration for asymmertic cells. Taken together, these data will be sufficient to enable Li transference numbers to be determined. This ongoing work will be pursued in collaboration with LBNL staff who are expert in this approach to measuring transference in solid polymer electrolytes. A new milestone for making these measurements will be included in the AOP and Task Status Reports for next year's work.

Other progress:



Scheme 1. Ionene lithium salts with a perfluorohexyl chain linking the imide anions.

Ionene salts with the general structure shown in Scheme 1 were synthesized at lengths corresponding to n=0 (monomeric LiTFSI), n=1 (dimer), n=3 (tetramer) and n=17 (oligomer). These salts are similar to those prepared earlier except that the linker group between imide anions is a perfluorohexyl in place of perfluorobutyl, as in the salts studied earlier in the project. In the course of making these salts, a general step-growth polymerization scheme for making ionene salts of discrete lengths was refined. This method will be the subject of a future publication.

Characterization. SPE's of the new ionene salts were prepared in PEG (2000 MW, crosslinked with an aryl tris isocyanate crosslinking agent) and their ionic conductivity measured at different temperatures. The trend in conductivity with ionene length is that conductivity is lowest for the salts with the longest ionene chains. These are also the salts that are expected to exhibit the highest Li transference, and future work will seek to establish how Li transference correlates with ionene length and linker length. We note also that there may be an effect of the PEG matrix crosslinking on the ionic conductivity, and to address this we will seek to make measurements in high-MW PEO to enable comparison with our earlier work on similar ionenes with perfluorobutyl chains linking imide anions.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith, University of Utah

TASK TITLE - PROJECT: Electrolytes - A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Lithium Cations in Polyether-based Solid Polymer Electrolytes

SYSTEMS: Li/polymer

BARRIER: Low ionic conductivity of the polymer electrolytes. Low Li battery power density.

OBJECTIVES: The primary objective is to understand influence of polymer structure on thermodynamics, kinetics and Li-ion transport in polymer electrolytes.

APPROACH: Our approach is to perform molecular dynamics simulations of poly(ethylene oxide), poly(oxymethylene oxide), poly(oxytrimethylene), and poly(propylene oxide) doped with $LiBF_4$ salt in order to understand the influence of polymer structure on thermodynamics, kinetics and Li-ion transport in polymer electrolytes. Force fields for interactions of Li^+/BF_4^- with poly(ethylene oxide), poly(oxymethylene), poly(propylene oxide) are based on high-level quantum chemistry calculations of model compounds.

STATUS OCT. 1, 2001: The project was initiated on January 15, 2002.

EXPECTED STATUS SEPT. 30, 2002: Force fields for interaction of poly(ethylene oxide), poly(methylene oxide), poly(propylene oxide) with $LiBF_4$ will be developed. Molecular dynamics simulations of poly(ethylene oxide)/$LiBF_4$ and poly(oxymethylene)/$LiBF_4$ will be carried out yielding structural properties of these polymer electrolytes, ion self-diffusion coefficients, conductivities, and transport numbers. Changes in the Li^+ transport mechanism will be correlated with changes in polymer structure.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over 10 year period, 1000 cycles.

MILESTONE:

a) 05/01/2002. Perform MD simulations of poly(ethylene oxide)/$LiBF_4$ using the developed potential, which includes many-body polarization effects. Validate developed potential by comparing conductivity, structure, and polymer dynamics with the available experimental data.

b) 09/01/2002. Develop potential energy functions for poly(oxymethylene), poly(oxytrimethylene), poly(propylene oxide) with Li^+ and BF_4^-. Perform conventional equilibrium MD simulations of poly(oxymethylene), poly(oxytrimethylene), and poly(propylene oxide) with Li^+ and BF_4^-. Study the effect of polymer dynamics and the strength of polymer-Li^+ interactions on ion transport.

c) 09/30/2002. Perform free energy calculations of Li^+ salvation in poly(ethylene oxide), poly(oxymethylene). Correlate free energies with polymer electrolyte structures and Li-ion transport.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

Parametric study of the influence of the strength of cation-polymer interactions and magnitude of the rotational isomerization barriers on structural and transport properties of PEO-based polymer electrolytes has been completed. Increase in the strength of the cation-polymer interaction was found to increase the fraction of "free" (e.g., uncomplexed by BF_4^-) Li^+ cations and decrease the cation self-diffusion coefficient while having little influence on ionic conductivity of PEO/$LiBF_4$ polymer electrolytes. This suggests that increase/decrease of the polymer-cation interaction while keeping other interactions unchanged is not the most promising strategy for improving conductivity of PEO-like polymer electrolytes. The magnitude of the conformational barriers, on the other hand, significantly influenced polymer and ion dynamics resulting in significant conductivity changes.

Quantum chemistry calculations have been performed on model compounds for poly(oxymethylene), poly(propylene oxide, poly(tetramethylene oxide) and their interactions with the Li^+ cation. Quantum chemistry based force fields have been developed for poly(oxymethylene)/$LiBF_4$, poly(propylene oxide)/$LiBF_4$, poly(tetramethylene oxide)/$LiBF_4$, and ethylene oxide-tetramethylene oxide (EO-OM_3) alternating copolymer doped $LiBF_4$. MD simulations to predicted thermodynamic and dielectric properties of poly(oxymethylene) is good agreement with the experiments. Slower polymer dynamics and higher ion aggregation in poly(oxymethylene)/$LiBF_4$ compared to poly(ethylene oxide)/$LiBF_4$ resulted in lower conductivity for the former.

MD simulations of ethylene oxide-tetramethylene oxide (EO-OM_3) alternating copolymer doped $LiBF_4$ have been initiated ahead of schedule in expense of free energy calculations for Li^+ solvation in order to compare with experimental findings for this technologically important alternating copolymer.

- **Further plans to meet or exceed milestones:**

In response to suggestions of the DOE reviewers, molecular modeling of gel electrolytes will be initiated. Quantum chemistry studies will be performed EC/$LiBF_4$ and EC/polyethers. The quantum chemistry data will be used for developing classical force fields for PEO-based comb-branched copolymer/$LiBF_4$/EC. MD simulations of PEO-based comb-branched copolymer/$LiBF_4$/EC gel electrolyte will be performed in order to understand the effect of the polymer matrix on cation transport and complexation in gel electrolytes. This work will be done in parallel to MD simulations of PEO-based comb-branched copolymer/$LiBF_4$ polymer electrolytes. Simulation results will be compared to experimental findings of John Kerr's group (LBNL).

- **Reason for changes from original milestones:**

The milestones have been changed in response to suggestion of DOE reviewers to initiate investigation of gel electrolytes.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-cost Li-ion, high-power Li-ion

BARRIER: Safety of Li-ion batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: The thermal stability of the ATD Program Gen 2 baseline electrolyte [1.2 M $LiPF_6$ in EC/EMC (3:7)] will be investigated by heating samples at 85˚C in sealed vials. Experiments will be conducted to determine the catalytic influence of cell components such as active electrode materials from the ATD Gen 2 chemistries on the thermal stability of the baseline electrolyte. Analytical techniques will be used to detect the presence of decomposition products from electrolytes in the presence of electrode materials. Capillary electrophoresis will be used to study Li salt degradation, and GC-MS will be used to study solvent degradation. Evidence suggests that the addition of an organic base such as pyridine reduces the decomposition rate of EC/DMC by limiting the disproportionation of $LiPF_6$. We plan to conduct further experiments with pyridine as an electrolyte additive. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss on carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing SEI layers.

STATUS OCT. 1, 2001: The polyether carbonates $(CH_2CH_2O)_mCOO)_n$ [PE_3C] were identified as possible decomposition products when 1 M $LiPF_6$ in 1:1 EC:DMC was heated to 85˚C. The PE_3C should simulate the end product that may be produced during the formation of the SEI layer (electrolyte decomposition) at the anode. The Illinois Institute of Technology (IIT) has evaluated PE_3C as an additive in 2016 coin cells (Li/carbon) containing 1 M $LiPF_6$-EC-DEC and the anode from ATD Program Gen 1 cells. Electrochemical studies showed that the presence of the electrolyte additive has a very small effect on the reversible capacity but produces a higher irreversible capacity loss. The negative electrodes from these coin cells were examined by TEM. There was no obvious difference in the SEI layer that was observed on graphite removed from cells with or without PE_3C additive. Pyrrole was investigated as an electrolyte additive. The irreversible capacity loss on graphite during the formation cycle was higher when pyrrole was present, suggesting it may have no benefit as an electrolyte additive.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete studies on the catalytic effect of active electrode components on the thermal stability of the ATD Gen 2 baseline electrolyte. The study of pyridine in altering the thermal stability of the ATD Gen 2 baseline electrolyte will be completed

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES: Complete analysis of the thermal stability of 1.2 M $LiPF_6$ in EC/EMC (3:7) containing pyridine as an electrolyte (3/02).

PROGRESS TOWARD MILESTONES

Pyridine stabilizes the thermal reactions of this electrolyte in the bulk of the solutions by intercepting the PF_5 formed from the salt. This then prevents the polymerization of the EC, no polymer is formed and no gas evolved. However, it is clear that there are reactions of the electrolyte with the electrodes that are complicated by the presence of the additive. No further work on this system is planned.

The effect of addition of additives such as vinylene carbonate (VC) into LP40 electrolyte, 1M $LiPF_6$-EC-DEC(1:1 w/w).

The addition of additives such as vinylene carbonate have been found to greatly improve calendar and cycle life in lithium ion batteries according to SAFT. It is generally thought that the reduction of the vinylene carbonate improves the behavior of the anode by forming a film on the electrode that reduces side reactions.

We have pursued an alternative scenario regarding the action of such additives. It is known that CO_2 is formed in Li Ion cells and this is reducible at the anode. The products of reduction of CO_2 in PC/R_4NClO_4 on carbon and copper are CO, carbonate and oxalate while on copper in the presence of water the formation of methane, ethane and ethylene has been reported. Reduction of CO_2 by means of a redox catalyst yields solely oxalate. A redox catalyst is an additive such as vinylene carbonate, methyl benzoate or dicyanobenzene that is able to pass electrons to the compound of interest in solution. Thus the redox catalyst is designated O and its reduced form R:

$$O + e^- \leftrightarrow R$$

$$R + CO_2 \leftrightarrow O + CO_2^{-\cdot}$$

$$2\, CO_2^{-\cdot} \rightarrow {}^-O_2C\text{-}CO_2^- \text{ (oxalate)}$$

The additive is recycled to the electrode and facilitates the reduction of the CO_2. This also occurs with EC and EMC but these compounds are reduced more slowly that CO_2. The oxalate is sufficiently soluble to reach the cathode where it can be re-oxidized to CO_2 resulting in a reversible self-discharge shuttle mechanism. The presence of additives such as VC can increase the reversible self-discharge mechanism at the expense of the irreversible self-discharge mechanism which results when CO_2 is reduced directly at the anode to CO and carbonate. Experiments are planned with the Cell Development task to measure reversible self-discharge and the effect, if any, of the addition of additives such as VC on this variable. Since reversible self-discharge is not thought to be involved in power fading and impedance rise, this mechanism represents a possible mode of action of VC in Li ion cells.

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li-ion cells

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point (>100°C), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V *vs.* Li); and (2) to carry out thermal investigations of the flame-retardant (FR) additives in Li-ion cells.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the Li-ion cells using differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2001: We completed the synthesis of the FR hexa-methoxy-tri-aza-phosphazene N_3P_3 $[OCH_3]_6$ and supplied this material to ANL for further testing in PNGV Li-ion cells. We also completed the mechanistic studies of the interaction of the HMTAP with the anode in Li-ion cells and observed the existence of the $Li\text{-}P(OCH_3)_2$ species on the electrode surface.

EXPECTED STATUS SEPT. 30, 2002: This project has been concluded on September 30, 2002. During this period, we have completed the electrochemical and thermal characterization of the flame-retardant additive HETAP in Li-ion cells using DSC and ARC. We have also completed the mechanistic studies of the FR additive HMTAP in Li-ion cell enviornment in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte during the requested extension of this project.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES: The electrochemical, thermal, and mechanistic studies of the new flame retardant HETAP in Li-ion cells have been completed as of September 2002.

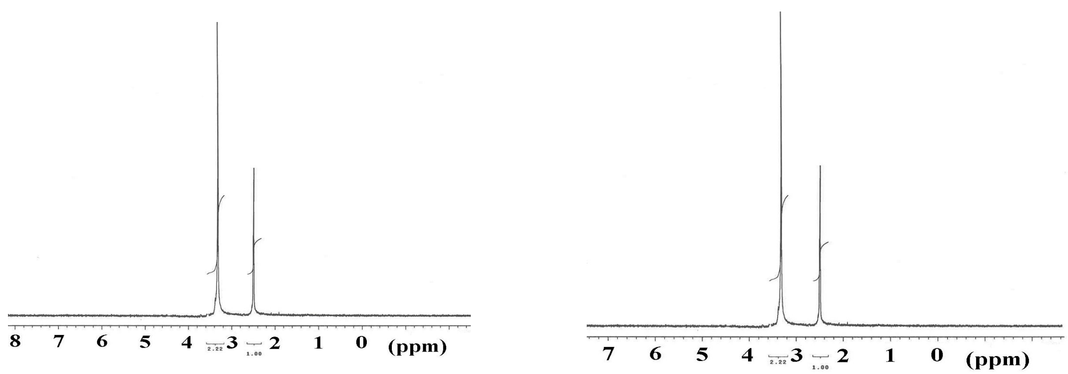
PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

1. A United States patent (**U.S. patent No. 6455200**) entitled "A Novel Flame-Retardant Additive for Li-ion Batteries" has been awarded to the Illinois Institute of Technology.

2. We also provided a total of 32 g of the flame retardant material (HMTAP) to the Electrovaya, Inc. (Canada) for its evaluation in their high capacity Li-ion cells. We were informed that the HMTP flame retardant additive showed excellent fire safety (70% success rate) in their high capacity Li-ion cells under nail penetration tests.

3 We have completed the spectral characterization of the carbon electrode in 1M $LiPF_6$ in EC-DMC (50:50 wt %), and the 10 wt % of HMTP. The carbon electrode was subjected to the potential of 10 mV (cathodic) and 4.2 V (anodic) vs. Li/Li^+ for 3 hr. After each experiment, the electrode surface was washed and scratched to obtain the adsorbed material FT-IT, EDS, ^1H NMR, and ^{31}P NMR investigations. Fig. 1 shows the ^1H NMR for the carbon electrode subjected to 10 mV (Fig. 1a) and 4.2 V (Fig. 1b) vs. Li/Li^+. One can clearly see the presence of the $-OCH_3$ group of the HMTP in ^1H NMR (δ=3.3 (*6 H*)) in Fig. 1a and Fig. 1b. In addition, a single peak in the ^{31}P NMR measurement (Fig. 2) also suggests that the HMTP is the source of the phosphorous signal. We also observed that the peak position shifts to the lower region compared to the pure HMTP. This shift suggests that Li is probably coordinated to P in the adsorbed film on the carbon electrode surface.



(a) **(b)**

Fig. 1 ^1H NMR spectra of the material removed from the carbon electrode surface (in 1M $LiPF_6$ in EC-DMC and the 10 wt % of HMTP) subjected to (a) 10 mV and (b) 4.2 V vs. Li/Li^+.

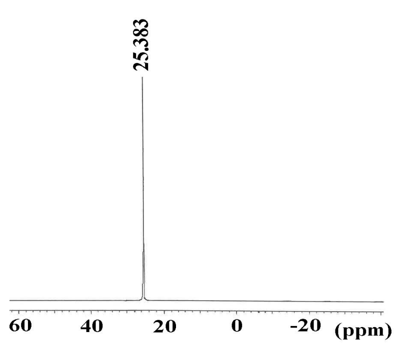


Fig. 2 ^{31}P NMR spectra of the material removed from the carbon electrode surface (in 1M $LiPF_6$ in EC-DMC and the 10 wt % of HMTP) subjected to 4.2 V vs. Li/Li^+.

- **The project is complete.**

BATT TASK 4
CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-cost (Li-ion) battery and Li-polymer battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel during electrochemical cycling, particularly those stabilized by a Li_2MnO_3 component, and those with a $LiMn_{1-x}M_xO_2$ composition (M=Ni, Co); for Li-polymer cells. The electrode material of choice is stabilized α-MnO_2.

STATUS OCT. 1, 2001: We exploited the concept of using a Li_2MnO_3 component to stabilize layered $LiMO_2$ structures with the ultimate objective of stabilizing layered $LiMnO_2$. In particular, we expanded our synthesis efforts to include solid solutions of $xLi_2MnO_3{\bullet}(1\text{-}x)LiMO_2$ compositions, where M = Mn, Ni, or Co, or a combination thereof. To date, these materials have yielded specific capacities of approximately 150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C, but for less than 100 cycles. Studies of $xLi_2MnO_3{\bullet}(1\text{-}x)LiMO_2$ compositions were initiated in which M′ = Ti, Zr, *i.e.*, with $Li_2M'O_3$ components that are isostructural with Li_2MnO_3.

EXPECTED STATUS SEPT. 30, 2002: Improvements in the electrochemical performance of $xLi_2MnO_3{\bullet}(1\text{-}x)LiMO_2$ electrodes will have been achieved with a targeted goal of 160 mAh/g for 100 cycles at 50 °C in Li-ion cells. Layered $LiMn_{1-x}M_xO_2$ compounds (M=Ni, Co), in particular $LiMn_{0.5}Ni_{0.5}O_2$ that yield 150 mAh/g for 50 cycles at 50°C in Li-ion cells will have been synthesized. Stabilized α-MnO_2 electrodes for Li-polymer cells will have been evaluated in collaboration with LBNL (J. Kerr); the targeted performance of these electrodes is 200 mAh/g for 100 cycles at 80°C. A detailed understanding of the structural/electrochemical property relationships in the above-mentioned electrode systems will have been gathered by a variety of techniques such as XRD, XANES, EXAFS, NMR, and HRTEM.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Synthesize and evaluate $LiMn_{1-x}M_xO_2$ compounds (M=Ni, Co) (April 2002); (b) achieve a technical target of 150 mAh/g for 50 cycles at 50 °C (June 2002); (c) achieve the targeted milestones for the performance of $xLi_2MnO_3{\bullet}(1\text{-}x)LiMO_2$ electrodes in Li-ion cells and for stabilized α-MnO_2 electrodes in Li-polymer cells (September 2002).

PROGRESS TOWARD MILESTONES

Accomplishments

Over the past two years, we have embarked on a strategy to develop stabilized structures with the general, "composite" formula $xLi_2M'O_3•(1-x)LiMO_2$ in which a layered rocksalt component, $Li_2M'O_3$, containing tetravalent ions such as Mn, Ti, or Zr, is used to stabilize a layered $LiMO_2$ component (M = Mn, Co, Ni) and to prevent the transformation to spinel during electrochemical cycling. In FY2002, we achieved our performance target for this class of electrode material (160 mAh/g for 100 cycles at 50 °C). In principle, it should be possible to synthesize similar compounds that yield higher electrochemical capacity, *i.e.*, ≥200 mAh/g.

The electrochemical reactivity of $0.05Li_2TiO_3•0.95LiMn_{0.5}Ni_{0.5}O_2$ at low voltage was investigated further (see previous report). This electrode shows good reversibility when cycled over a wide voltage range (4.3 or 4.6 to 1.25 V, Fig. 1). The discharge capacity of $0.05Li_2TiO_3•0.95LiMn_{0.5}Ni_{0.5}O_2$ was 260 mAh/g after 10 cycles at 50 °C.

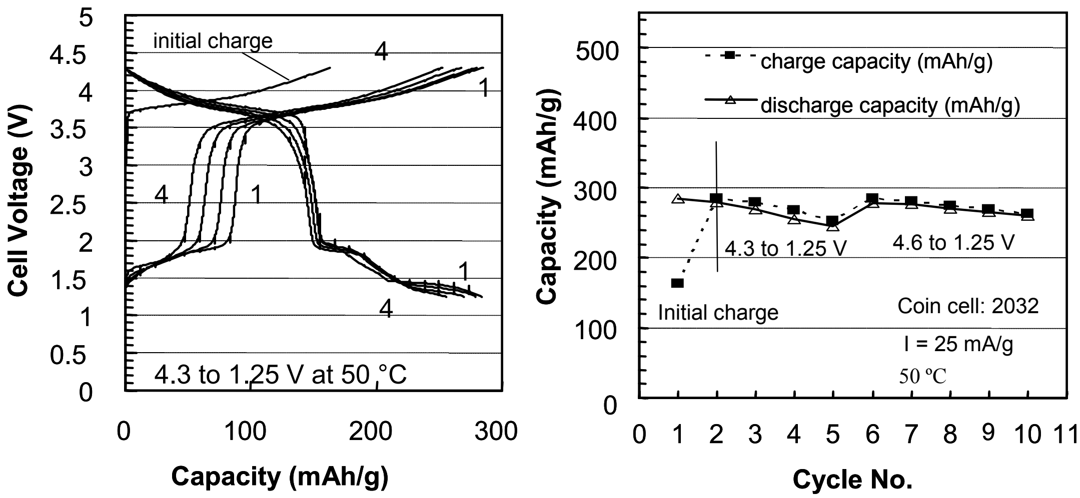


Figure 1. Electrochemical data of a $Li/0.05Li_2TiO_3•0.95LiMn_{0.5}Ni_{0.5}O_2$ cell.

It is believed that in such "composite" structures the Li_2TiO_3 component forms clusters or domains within the $LiMn_{0.5}Ni_{0.5}O_2$ structure. Since domains of Li_2TiO_3 would share a common rigid oxygen framework with $LiMn_{0.5}Ni_{0.5}O_2$ domains, then the composite formula $0.05Li_2TiO_3•0.95LiMn_{0.5}Ni_{0.5}O_2$ could be expressed alternatively as $(Li_{1.0})_{3a}(Li_{0.05}Ni_{0.475}Ti_{0.475})_{3b}O_2$, the latter formula identifying the cations in alternate 3a and 3b layers. The monoclinic distortion from trigonal symmetry that is observed in $0.05Li_2TiO_3•0.95LiMn_{0.5}Ni_{0.5}O_2$ electrodes is consistent with the clustering of Ti atoms; this distortion would be absent in a $(Li_{1.0})_{3a}(Li_{0.05}Ni_{0.855}Ti_{0.095})_{3b}O_2$ structure if the cations were randomly distributed within the 3b layer. The low voltage reaction is reversible. Other layered electrodes such as $LiMnO_2$ or $LiNi_{0.8}Co_{0.2}O_2$ do not show similar behavior.

In new developments, modified spinel ($LiMn_2O_4$) and layered $0.03Li_2TiO_3•0.97LiMO_2$ (M=Mn, Ni, Co, or Al) electrodes are being evaluated.

Further plans to meet or exceed milestones: Although we deemphasized our efforts on lithium-polymer cathodes in FY2002 because of budget/manpower constraints, we hope to be able to restart these efforts in the future.

Reason for changes from original milestones: With budget/manpower constraints, we focused our efforts during FY2002 entirely on Li-ion- rather than Li-polymer cathodes.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2001: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can also be stabilized by the addition of Mn ions, and that lithium iron phosphate can be synthesized very rapidly in a hydrothermal reactor.

- Layered $Li_xCo_yMn_{1-y}O_2$: ≥200 Ah/kg for 8 cycles, and stabilized Li_xMnO_2 ≥ 150 Ah/kg for 6 cycles.
- Layered $Mn_{0.1}V_2O_5$; ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2002: For low-cost Li-ion cells, we expect to identify the changes in $LiMnO_2$ structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized $LiMnO_2$ and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized δ-vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade. We will also have determined the feasibility of using a hydrothermal approach to the manufacture of lithium iron phosphate.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are: (a) to characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg, (b) complete the characterization of manganese stabilized vanadium oxides and (c) to compare the best samples with iron phosphates for polymer or gel batteries by July 2002.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestones over last quarter:
(a) Stabilized Manganese Oxide Cathodes
Major emphasis continues to be placed on the electronic stabilization of layered manganese oxide, such as exemplified by the compound $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$.A range of compositions have been studied, and the first discharge capacity was proportional to the nickel content suggesting that the redox active specie is nickel which cycles between Ni^{2+} and Ni^{4+}. The charging regime for the cobalt is mostly above the 4.3 to 4.4 volt cut-off used here. To better understand the redox processes occurring, XPS and magnetic studies have been initiated. The susceptibility data is consistent with either Ni(III) + Mn(III) or Ni(II) + Mn(IV). The available literature data (from the Nesper group on $LiMn_{0.5}Ni_{0.5}O_2$) is inconsistent with the present ideas on the redox couple; initial interpretation of our XPS data (L. Matienzo of IBM) is underway We see changes in the oxygen spectrum between different samples, but not between the Ni, Mn or Co spectra. The spectra for the phase $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ are shown below. Discussions were held with G. Ceder during the last quarter on these materials.

(b) Iron Phosphate Cathodes
We are nearing completion of our study on the $LiFePO_4$ base case cathode, which we will use for comparison against other cathodes such as the layered manganese nickel compounds discussed above.

Studies are continuing on other iron phosphate phases, both crystalline and amorphous. The Giniite phase is undergoing characterization at Binghamton and at Stony Brook (Clare Grey), and offers the opportunity for extensive exchange of the iron for other metals such as manganese.

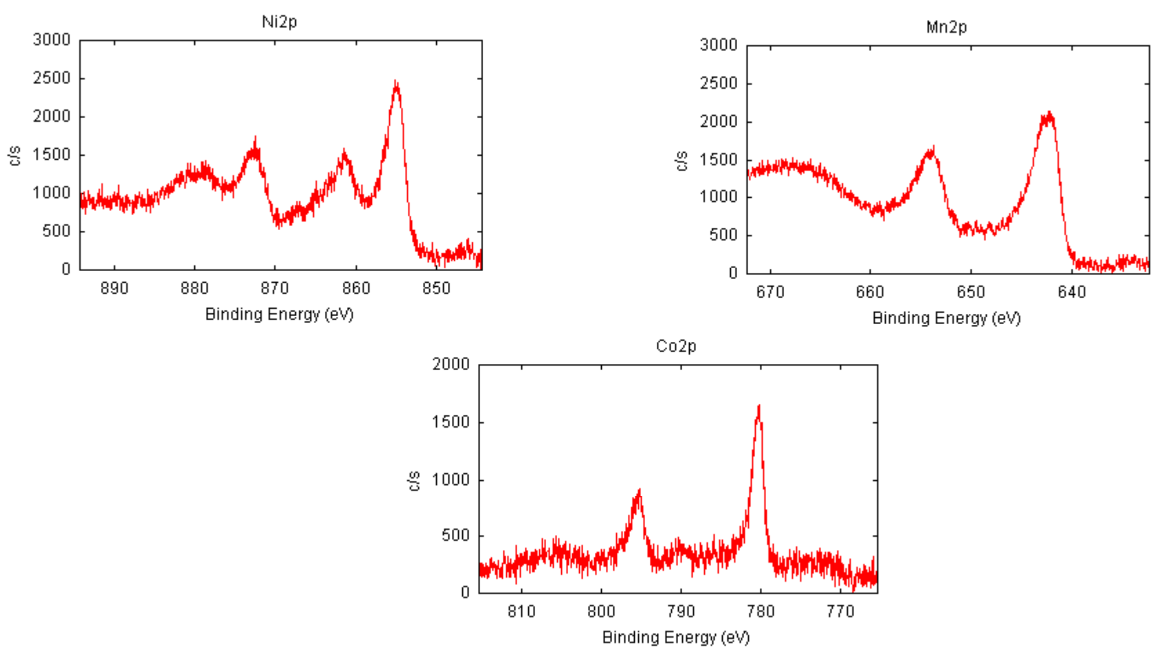


Figure 1. XPS spectra of $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$.

- **Further plans to meet or exceed milestones:** N/A
- **Reason for changes from original milestones:** N/A

Publications:
Y. Song, S. Yang, P. Y. Zavalij and M. S. Whittingham: Temperature-dependent properties of $FePO_4$ cathode materials, *Mater. Res. Bull.*, **37** 1249-1257 (2002).

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.,* manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.,* sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2001: A milestone to provide $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.98}S_{0.02}$ to the BATT program in fall 2001 was met and samples of tunnel-containing Li_xMnO_2 were also provided. Several synthetic approaches for producing $LiFePO_4$ were evaluated, and sol-gel was considered the most promising.

EXPECTED STATUS SEPT. 30, 2002: Initial screening of novel P2-substituted layered manganese oxides will be completed, and a go/no go decision made based on the results. Recommendations will be made on the appropriateness of selected cathode materials for the BATT program. A design for an *in situ* x-ray diffraction cell will be finished.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:
1) Provide samples of conventional $LiFePO_4$ or sol-gel synthesized $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.97}S_{0.03}$ to the BATT program for testing (11/01): **completed**
2) Design *in situ* x-ray diffraction cell for structural studies of Li_xMnO_2 (6/02)
3) A Li/tunnel MnO_2 cell has been fabricated for an *in situ* XRD experiment at Sandia National Laboratory (Livermore, CA) using their cell holder design. Appropriate changes will be made to the design based on the outcome of the test.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

A "go" decision has been made to continue work on layered O2 manganese oxides substituted with Ni, Co, or Al, based upon their high discharge capacities (180 mAh/g).

The electrochemical and structural properties of O2-$Li_xM_{0.11}Mn_{0.89}O_2$ (M=Al, Fe, Co, Ni, Cu, Zn) were studied. Stepped potential experiments (near equilibrium conditions) on $Li/Li_xNi_{0.11}Mn_{0.89}O_2$ and $Li/Li_xAl_{0.11}Mn_{0.89}O_2$ cells show reversible capacities of 180 mAh/g, with the expected diffusional behavior between 3.8 and 2.0 V (Fig. 1). Cells containing O2-$Li_xM_{0.11}Mn_{0.89}O_2$ where M=Al, Co or Ni delivered up to 160 mAh/g on the first discharge (Fig. 2), but for M=Zn, Cu, or Fe, only about 80 mAh/g was obtained. In some cases, reducing the current density improved utilization, implying kinetic limitations. Less capacity fading upon cycling was seen for M=Ni, Al than for M= Co. Postmortem analyses (XRD, ^{7}Li MAS-NMR by Y. J. Lee) on electrodes indicated that no structural changes occurred during cycling, contrary to previous reports by Dahn et al. Based on the good stability and high capacities of some of these electrodes, we have decided to continue work on them. Future experiments include varying the substitution levels (y in $Li_xM_yMn_{1-y}O_2$) to monitor the effect on discharge characteristics. Materials highly substituted with Ni are of particular interest, since a high capacity layered $LiMn_{0.5}Ni_{0.5}O_2$ compound (although with a different stacking sequence) has recently been reported.

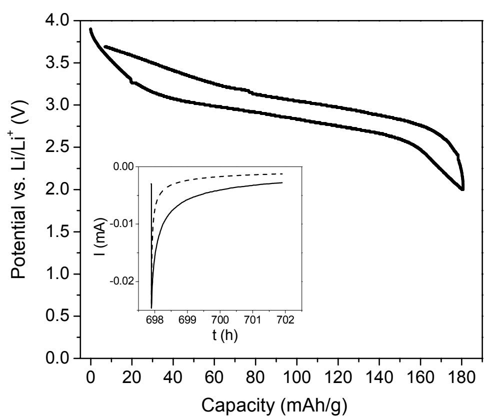


Figure 1. Pseudo-open circuit voltage profile obtained by a potential step experiment on a Li/1M $LiPF_6$ EC-DMC/$Li_xAl_{0.11}Mn_{0.89}O_2$ cell. The inset shows a current vs. time trace for one 10 mV step with a Cottrell equation fit (dashed line) offset for clarity, indicating diffusional behavior.

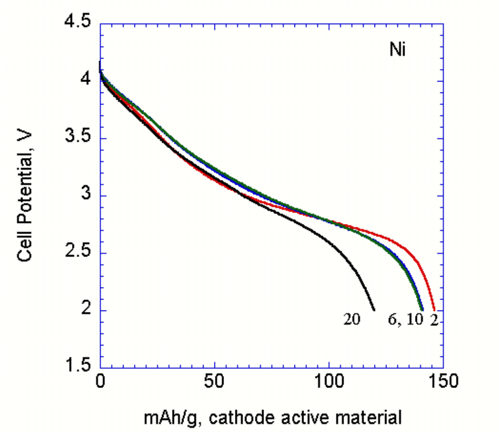


Figure 2. Galvanostatic discharges at 0.05 mA/cm^2 of a Li/1M $LiPF_6$ EC-DMC/$Li_xNi_{0.11}Mn_{0.89}O_2$ cell. The cycle numbers are labeled.

Further plans to meet or exceed milestones N/A

Reason for changes from original milestones N/A

PUBLICATIONS

1) M.C. Tucker, M.M. Doeff, T.J. Richardson, R. Fiñones, E.J. Cairns and J.A. Reimer, "Hyperfine Fields at the Li Site in $LiFePO_4$-Type Olivine Materials for Lithium Rechargeable Batteries: A ^{7}Li MAS NMR and SQUID Study," *J. Am. Chem. Soc.*, **124**, 3833 (2002).

2) M.M. Doeff, J. Hollingsworth, and J.-P. Shim, "Factors influencing the Electrochemical Behavior of Sulfur-doped Aluminum-substituted Lithium Manganese Oxide Spinels in Lithium Cells," *Electrochem. Soc. Meeting*, Philadelphia, PA 2002, Vol 2002-1, abstract number 825.

3) T.A. Eriksson and M.M. Doeff, "A Study of Layered $Li_xM_yMn_{1-y}O_{2+z}$ (M=Fe, Co, Ni, Zn, Al) Cathode Materials, " *11th International Meeting on Lithium Batteries*, Monterey, CA 2002, abstract number 75.

TASK STATUS REPORT

PI, INSTITUTION: J. Evans and T. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Aluminum in Li Cell Electrolytes

SYSTEMS: High-power Li-ion battery

BARRIER: Limitations on cycle or "shelf" life.

OBJECTIVES: The primary objective is to quantify corrosion of aluminum when used in present or candidate Li cell electrolytes. Aluminum is a relatively inexpensive material that is widely used for the positive electrode current collector and cell containment.

APPROACH: The approach uses an electrochemical quartz crystal microbalance (EQCM) to determine the initial rates of corrosion of Al in BATT electrolytes as a function of potential and to discover whether passivation occurs. One of the Li salts ($Li(CF_3SO_2)_2N$) of the three baseline chemistries has been shown to corrode Al in prior LBNL work. Experiments on coated Al samples and longer term experiments (where exposed samples are examined at the scanning electron microscope) will also be conducted. As newer electrolytes (with higher performance characteristics or minimal CO_2 venting problems) are discovered their corrosivity to Al will be determined.

STATUS OCT. 1, 2001: No recent work on this project.

EXPECTED STATUS SEPT. 30, 2002: EQCM/cyclic voltammetry measurements completed on pure and carbon-coated Al samples in contact with three electrolytes most relevant to the BATT Program.

RELEVANT USABC GOALS: Cycle life >500 cycles.10-year life, <20% capacity fade over a 10-year period.

MILESTONE:
July 31: Measurements of the corrosion of Al in $LiPF_6$ + PC:EC:DMC(1:1:3) completed using the EQCM.
Sept. 30: Measurements of the corrosion of Al in $Li(CF_3SO_2)_2N$ + PEGDME (PEO analog) completed using the EQCM.

PROGRESS TOWARD MILESTONES

Figure 1 clearly shows that the presence of $LiBF_4$ in LiTFSI electrolyte significantly suppressed the corrosion current, and no corrosion is observed when 0.5M $LiBF_4$ was added. The complicated mass change of increase-decrease-increase in LiTFSI solution indicates deposition (or adsorption) of precipitates occurring at the first anodic scan, but some dissolution (desorption) of the precipitates at the beginning of cathodic scan followed by accumulation of precipitates. Mass accumulation is pronounced with increased $LiBF_4$ content. Although the massper electron (mpe) change during cycling does not match with mpe values of any expected deposited species, the calculated mpe of -227 on anodic scan when 0.5M $LiBF_4$ was present reflects that large sized precipitates deposited on the surface of Al.

Surface chemistry of Al has been carried out by employing FTIR spectroscopy. In Fig. 2(a) and (b), peaks at 1371, 1157 and 1195 cm^{-1}, assigned to $\nu_a(SO_2)$, $\nu_s(SO_2)$ and $\nu_a(CF_3)$ respectively, must be of trifluorosulfonimide ($TFSI^-$, $N(SO_2CF_3)_2^-$), indicating that corrosion products include this functional group. The broad peak around 3311 cm^{-1} reveals the presence of OH^-. Fig. 2(c) shows peaks at 2925, 2854, 1605 of ν_s(CH), ν_a(CH) and ν(C=O), respectively, are clearly shown together with other peaks from organic species. Apparently, the passivation layer consists of much organic species. In particular, the peak at 1065 cm^{-1} is attributed to some B-F bonding, and the very sharp peak at 3676 cm^{-1}, corresponding to ν(OH), indicates the presence of free LiOH. Based on both the FTIR spectral findings and EQCM results, as well as considering steric hindrance raised by large size of $N(SO_2CF_3)_2^-$ anion and the presence of OH^-, we suppose that the corrosion products present on Al after the experiment with LiTFSI/EC+DMC would be $Al[N(SO_2CF_3)_2]_{3-x}(OH)_x$ and little organic species. On the other hand, passivation products are thought to be a comprised of organic species such as $ROCO_2Li$, Li_2CO_3, LiOH, and B-F bonding containing salt. Use of mixtures of these two Li salts might be efficient in increasing the corrosion resistance of Al current collectors and improving the performance of Li-ion batteries.

We have met the first April milestone but have not completed the second work with PEGDME. Dr. Xueyuan Zhang, hired as a postdoc in October, 2002, has become involved in this project. The corrosion status of Al as the current collector in the coin battery is being determined. The growth rate of Al corrosion in different BATT electrolytes also will be determined.

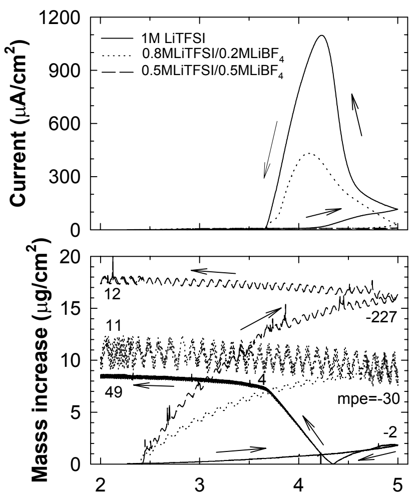


Figure 1. Comparative plots of cyclic voltammograms and the corresponding mass increase for the Al at the first cycle in 1M LiTFSI/EC+DMC, 0.8M LiTFSI + 0.2M $LiBF_4$/EC+DMC and 0.5M LiTFSI + 0.5M $LiBF_4$/EC+DMC; sweep rate = 5 mV/s .

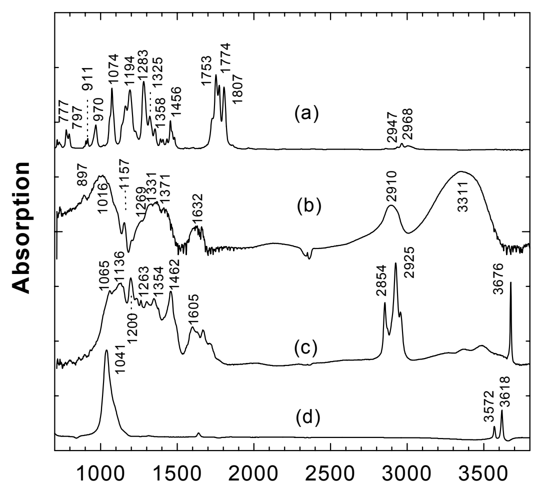


Figure 2. FTIR spectra of (a) 1M LiTFSI/EC+DMC electrolyte solution, and of Al after CV-EQCM (b) in 1M LiTFSI/EC+DMC, (c) in 0.8M LiTFSI + 0.2M $LiBF_4$/EC+DMC and of (d) $LiBF_4$ salt.

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a Li-ion battery that operates between Ni(II) and Ni(IV).

APPROACH: Layered $LiMO_2$ oxides have been shown to exhibit a high Li^+-ion mobility once a fraction of the Li is removed. On the other hand, these oxides are metastable and decompose on removal of a large fraction of Li from between the host MO_2 layers. $LiNi_{0.5}Mn_{0.5}O_2$ contains Mn(IV) and removal of Li operates on the Ni(III)/Ni(II) and Ni(IV)/Ni(III) couples, both of which are pinned at the top of the O^{2-}:$2p^6$ band. Ohzuku and Mikimura have demonstrated a capacity over the range 2.5 to 4.3 V *vs* Li that approaches 150 m Ah/g for 30 charge/discharge cycles at room temperature. We have found that the capacity decreases sharply at higher current densities, which we suspect is the result of poor conductivity. We will investigate (1) whether we can increase the capacity at higher current densities by coating the particles with carbon and (2) the role, if any, of the Mn(IV) ions. Since small particle sizes are probably necessary, sol-gel synthetic routes will be employed.

STATUS OCT. 1, 2001: New project initiated 4/2/02.

EXPECTED STATUS SEPT. 30, 2002: Preliminary data.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: (due in FY 2003)

Testing influence of carbon coating on layered and spine Ni^{2+}, Mn^{4+} compounds operating on Ni^{3+}/Ni^{2+} and Ni^{4+}/Ni^{3+} couples. Testing influence of ZnO as getter for HF in cells requiring $LiPF_6$ as the electrolyte.

PROGRESS TOWARD MILESTONES

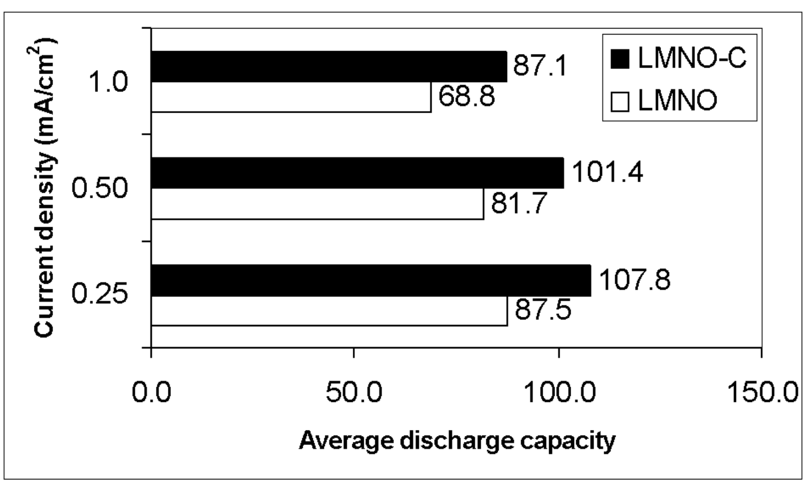
- **Accomplishments toward milestone over last quarter:**

$LiMn_{0.5}Ni_{0.5}O_2$ has a face-centered-cubic oxygen array with Li^+ occupying alternate (111) planes of octahedral sites and $Mn_{0.5}^{4+}Ni_{0.5}^{2+}$ occupying the other planes of edge-shared octahedral sites. The Li^+ ions can be reversibly extracted electrochemically (or chemically); extraction of the first 0.5 Li/formula unit oxidizes the Ni^{2+} to Ni^{3+}; further extraction of Li oxidizes Ni^{3+} to Ni^{4+}. Because the Ni^{3+}/Ni^{2+} redox couple is pinned at the top of the O-2p bands, there is a smooth transition of the electrochemical potential on passing from the NI^{3+}/Ni^{2+} to the Ni^{4+}/Ni^{3+} couple. However, the 90^o Ni-O-Ni interactions and the marginally percolation pathways for the Ni atoms result in a poor electronic conductivity, which limits the power capability of the material as a cathode in a rechargeable Li^+-ion battery. We have, therefore, investigated the use of Li^+-permeable carbon coating that can supply electrons to the interior of the cathode particles to charge-balance Li^+-ion insertion.

The carbon source for coating the oxide particles was a carbon xerogel formed from a resorcinol-formaldehyde (R-F) polymer. The $LiMn_{0.5}Ni_{0.5}O_2$ particles were carbon coated by compacting into a pellet a mixture of the oxide and R-F in an 85:15 weight ratio. Li was extracted chemically from the pellet with excess I_2 in an acetonitrile solution. The products were characterized structurally by powder x-ray diffraction and then combined with acetylene black and teflon in a 70:25:5 weight ratio and rolled into sheets from which cathodes were cut.

Button-type electrochemical test cells used a Li anode and 1M $LiPF_6$ in 1;1 ethylene carbonate: diethyl carbonate as the electrolyte. Comparison was made between the performances of cells with coated and with uncoated oxide particles. The carbon content of the coated particles was 2.5% (w/w) determined by thermogravimetric analysis. Scanning electron microscopy images showed that both the coated and uncoated oxides contained 10-100 nm particles bound into 10-150 micron agglomerates. A carbon map obtained with an energy-dispersive x-ray spectrometer showed the carbon coating was evenly distributed across the agglomerate surfaces.

The discharge curves showed voltages ranging from 4.1 to 3.5 V versus Li; the figure compares the discharge capacities for cathodes with coated vs. uncoated oxide agglomerates. Although the carbon coating gave a definite improvement in capacity, the performance does not compete with that of $LiFePO_4$. If agglomeration can be avoided, a better result may be obtained.



- **Further plans to meet or exceed milestones** N/A
- **Reason for changes from original milestones** N/A

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology
C.P. Grey, State University of New York at Stony Brook

TASK TITLE - PROJECT: Diagnostics - NMR and Modeling Studies

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a lithium-ion battery that operates between Ni(II) and Ni(IV).

APPROACH: Use solid state NMR and XAS to characterize local structure and oxidation states of the nearby cations (in the 1st and 2nd cation coordination spheres) as a function of state of charge and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure on cell voltages and to identify promising cathode materials for BATT applications. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate the effect of doping on conductivity.

STATUS OCT. 1, 2001: New project initiated 4/2/02

EXPECTED STATUS SEPT. 30, 2002: Preliminary Data

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:
1) Attend BATT Review, July 1-2, 2002, at LBNL -complete.
2) Determine the site energies and voltages of the different Li environments in (1–x) $Li[Ni_{0.5}M_{0.5}]O_2$. x $Li[Li_{1/3}M_{2/3}]O_2$ (M = 4+) by first principles calculations. 9/30/02 - complete.
3) Determine the Li local environments and Ni oxidation state as a function of state of charge in (1–x) $Li[Ni_{0.5}M_{0.5}]O_2$. x $Li[Li_{1/3}M_{2/3}]O_2$ (M = 4+) by NMR spectroscopy and XAS. 9/30/02 - complete.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

Two compositions, $Li[Ni_{0.5}Mn_{0.5}]O_2$ and $Li[Li_{1/9}Mn_{5/9}Ni_{3/9}]O_2$, were investigated by NMR. ^6Li NMR results clearly showed the presence of Li ions in both the Li and transition metal (T. M.) layers of these layered materials, in *both* systems. The NMR results for $Li[Ni_{0.5}Mn_{0.5}]O_2$ are consistent with Ni^{2+} substitution into the Li layers as found in $LiNiO_2$. The Li local environments in the T. M. layers resemble the Li environments in the manganese layers of Li_2MnO_3 and can be represented by the local environment $Li(OMn)_{6-n}(ONi)_{n,}$ where $n \leq 1$. These NMR are confirmed with Mn and Ni EXAFS studies performed in collaboration with Dr. J. McBreen's group at BNL, which show that the manganese ion local environments contain a larger number of Li ions than the Ni-ion local environments.

First principles calculations have been performed on (1–x) $Li[Ni_{0.5}Mn_{0.5}]O_2$. x $Li[Li_{1/3}Mn_{2/3}]O_2$ and show that the environments for Li in the T.M. layers surrounded by more Mn ions are more stable than those surrounded by more Ni ions and that Li doping in the T.M. layers reduces the tendency for Ni incorporation in the Li layers. A more detailed analysis of the Ni-Mn-Li arrangements in these materials is underway. Both the 1st principles calculations and XAS experiments show that the redox process involves nickel, the manganese ions remaining as Mn^{4+} during the 1st charge cycle at 4V.

The NMR results for both compositions clearly demonstrate that the Li is removed from both the Li layers and the T.M. layers on cycling. Calculations were performed in order to understand this phenomenon in more detail and showed that Li is removed from the Li and T.M. layers at similar potentials. The latter process is facilitated by Li vacancies in the T.M. layers. Li NMR showed that the Li ions return to the T.M. layers on discharging and that the process is reversible (Fig. 1).

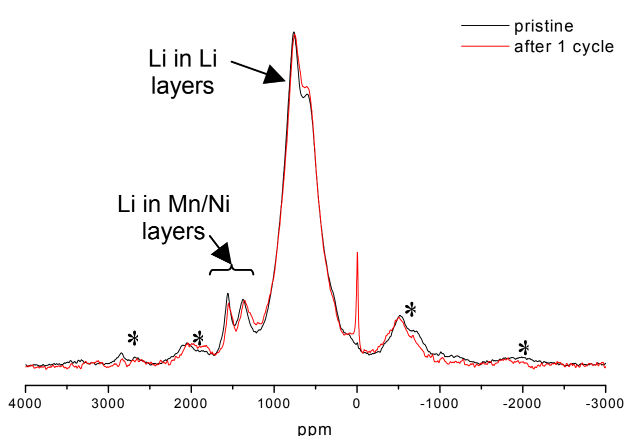


Figure 1. ^6Li MAS NMR of $Li[Li_{1/9}Mn_{5/9}Ni_{1/3}]O_2$ shows that Li in both the Li-layers and transition metal layers is removed but then returns following the 1st charge cycle.

- **Further plans to meet or exceed milestones:** N/A

- **Reason for changes from original milestones:** N/A

BATT TASK 5
DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon and R. Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

APPROACH: Use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Our goal is to identify changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2001: We identified changes in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode surface chemistry which accompanied cycling in $LiPF_6$-EC-EMC electrolyte, and identified surface carbon loss as a potential cell degradation mode.

EXPECTED STATUS SEPT. 30, 2002: We expect to provide detailed characterization of surface processes (including changes in surface morphology, near-surface structure, chemistry, and SEI growth) on BATT Program $LiFePO_4$ cathodes and model thin-film $LiMn_2O_4$ cathodes.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONE: (a) Determine the effect of sulfur and Al additives on the structure, surface morphology and chemistry of $LiMn_2O_4$ electrodes (January 2002). (b) Characterize surface processes such as changes in surface morphology, chemistry, and SEI formation on $LiFePO_4$ and $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.97}S_{0.03}$ model thin-film cathodes (June 2002).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone (b) over last quarter: Our characterization of composite $LiFePO_4$ cathode surface processes showed that particles of active material are almost entirely coated by a layer of amorphous carbon. Raman spectra of charged and discharged material exhibited distinct spectral characteristics that correspond to two different phases, as expected. We observed carbon recession from the cathode surface during cycling, and we identified particles of $LiFePO_4$ that remained in a charged state despite deep discharge at the end of cell testing. Phosphorous compounds were also detected locally on the electrode surface. Their origin and mechanism of formation are currently under investigation.

In situ spectroscopic ellipsometry was used to investigate the formation and growth of SEI layers on thin-film $LiMn_2O_4$ cathodes. First, we confirmed that a SEI layer formed as soon as the cathode came into contact with the electrolyte (1.0 M $LiPF_6$ in EC/DMC), as signaled by a sharp change of ellipsometric data when electrolyte was injected into the electrochemical cell. To account for the observed change, it was necessary to include in our model a SEI layer between the cathode and electrolyte. Figure 1 shows that our physical model in which a SEI layer is included fit the ellipsometric data very well. By analyzing the ellipsometric data and calculating the resulting SEI optical constants, we found that SEI layer developed slowly during the first few cycles. The SEI layer optical constants for the 4th cycle were almost identical to those for the 3rd cycle, which indicates that SEI layer composition had reached at a stable state.

This completes our work on Milestone (b).

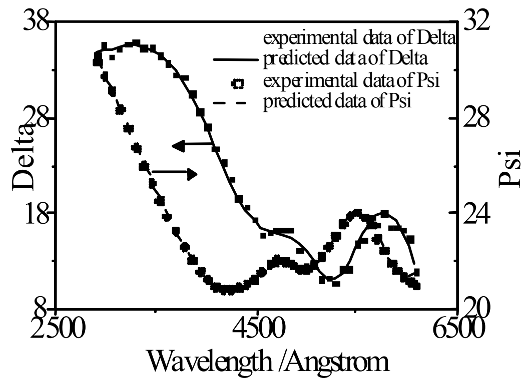


Figure 1. A model of the cathode/electrode interface agrees with experimental ellipsometry data very well when a SEI layer is included in the model. Left-hand ordinate – Delta(deg). Right-hand ordinate – Psi(deg).

Additional accomplishments

We have already reported the use of Raman microscopy and atomic force microscopy (AFM) to monitor the effect of structural changes that occur in graphitic materials upon extensive cycling at elevated temperatures. During the past quarter we carried out a detailed qualitative analysis of the inorganic products that formed on the disordered part of the graphite anode. The strong peak at $1087 cm^{-1}$ corresponds to the spectral signature of Li_2CO_3, and a broad band centered at $1120 cm^{-1}$ is characteristic for lithium polyphosphates. These products were formed by side reactions on the anode surface, and they caused a permanent shift in Li inventory and contributed to the observed capacity loss in BATT Program baseline cells.

We completed our analysis of power fade mechanism of baseline $LiAl_{0.05}Ni_{0.8}Co_{0.15}O_2$ cathodes at elevated temperatures. Based on our Raman microscopy data analysis and current-sensing AFM imaging results, we concluded that active material particle isolation is most likely responsible for the observed power and capacity loss in cathodes cycled at 60^oC. The mechanism of electronic conductivity loss within the composite cathode, which coincides with observed retreat of carbon additives, requires better understanding and will be the subject of further work.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM).

STATUS OCT. 1, 2001: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel $LiMn_2O_4$ cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of $LiMn_2O_4$ cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete our investigation of $LiMn_2O_4$ at 55°C. We also expect to complete our work on XAS at the P K-edge and its use in detection of electrolyte decomposition products. This will include application of the technique in the ATD Program. The cathode studies will include work on high capacity materials such as $LiFePO_4$ and substituted layered $LiMnO_2$.

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (1) Complete stability studies of $LiMn_2O_4$ in LiF based electrolytes, at 55°C, by April 30, 2002. (2) Complete work on XAS at the P K-edge and apply it to materials from the ATD program by August 31, 2002. (3) Complete *in situ* XAS and XRD studies of $LiFePO_4$ and substituted layered $LiMnO_2$ by December 31, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments towards milestone over last quarter:** The work on $LiMn_2O_4$ spinel cathodes has been completed and was reported in the Quarterly Report submitted in April 2002,.

- **Further plans to meet or exceed milestones** The milestone is completed.

- **Reason for changes from original milestones**

  Because of the limited energy density no work was done on $Li_{1.02}Al_{.25}Mn_{1.75}O_{3.97}S_{0.03}$.

- **Accomplishments towards milestone over last quarter**: The work on XAS at the P K-edge was completed in the Third Quarter and the results were reported at both the BATT and ATD Merit Reviews. The technique is now being applied to study phosphorous containing species in both anodes and cathodes from cycled and abused Gen-2 cells.

- **Further plans to meet or exceed milestones:** The milestone was completed ahead of schedule because we did not experience the problems and delays that we usually encounter in this type of work.

- **Reason for changes from original milestones:** N/A

- **Accomplishments towards milestone over last quarter**: A paper on *in situ* XRD studies on a carbon coated Si anode material that was obtained from Prof. Yoshio of Saga University has been accepted for publication in Electrochemical Communications. Extensive XRD work has been done on substituted layered $LiMnO_2$ that was obtained from two sources. In conjunction with SUNY Stony Brook extensive *in situ* XRD and x-ray absorption spectroscopy (XAS) and *ex situ* NMR was done on a Ni substituted layered $LiMnO_2$ material. This will be reported in the report from SUNY Stony Brook. Extensive *in situ* XRD and XAS was done on the second carbon coated $LiFePO_4$ obtained from Hydro Quebec.

- **Further plans to meet or exceed milestones** It is anticipated that the milestones will be met on time.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g*., using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2001: Used Density Functional Theory (DFT) to calculated oxidation potentials of different Li-ion battery electrolytes and additives.

EXPECTED STATUS SEPT. 30, 2002: Together with other members of the project, establish thermal and electrochemical stability of different Li-ion battery electrolytes and additives as a function of the state of charge using ATD Program Gen 2 electrode materials.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:
1. Determine onset potential for gas evolution from cathode materials as a function of composition of the electrolyte and the cathode material. (6/02)
2. Determine the kinetics of thermochemical reactions between the electrolyte and cathode materials as a function of temperature and composition. (9/02)

PROGRESS TOWARD MILESTONES

No progress to report.

TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-ion and Li-polymer batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling. Use this information to understand capacity fade, and to design new electrode materials.

APPROACH: Our approach is to use ^{7}Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. NMR data on model failure mechanisms will be used to interpret the spectra. Structural information and information on the local Li environment will be gathered to improve our ability to design new electrode materials.

STATUS, OCT. 1, 2001: We compared ^{7}Li MAS NMR spectra for stoichiometric and substituted tunnel-structure manganese oxides after electrochemical cycling. This information helps to elucidate the structural changes accompanying capacity fade. We initiated NMR analysis of fresh $LiFePO_4$-based materials, and began long-term cycling experiments on these materials.

EXPECTED STATUS SEPT. 30, 2002: We expect to have compared ^{7}Li MAS NMR spectra for a range of $Li(Mn,Fe)PO_4$ materials and Gen 2 electrodes at various states of charge. Cycled tunnel-structure materials will have been examined by MAS NMR for structural changes. The results will be helpful in interpretation of NMR spectra of cycled electrodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to
(1) Compare NMR-observable properties of baseline and novel electrodes, 9/02,
(2) Measure capacities, capacity fading in our synthesized intermetallics, 6/02,
(3) Use NMR to determine structural changes that cause capacity fade, 8/02.

PROGRESS TOWARDS MILESTONES

- **Accomplishments toward milestones during last quarter:**

Layered $Li_y[Al_{0.11}Mn_{0.89}]O_2$ with an O2-type structure was studied with ^{7}Li MAS NMR after electrochemical cycling. After the electrode was charged to 4.3 V and discharged to 2.0 V, the cell was charged again and disassembled for the NMR experiments. The spectra of the fresh electrode and the electrode after one cycle are very similar (as shown in Fig. 1A, curves (b) and (c)). Resonances at 700, 145 and 0 ppm were observed, which were assigned to Li cations in the O2 environment, O3 environment, and on the grain surface, respectively. This indicates that there were no discernible changes in the structure before and after cycling, which is contrary to the previous reports by Dahn et al. After 62 cycles, Li in the O2 environment produced a resonance at a lower frequency with a higher intensity than in the fresh electrode (Fig. 1B). This indicates that the electrode did not undergo significant structural changes during cycling. The increased intensity is probably due to the slightly lower state of charge for the electrode.

We also obtained the spectra of a $LiAl_{0.05}Ni_{0.80}Co_{0.15}O_2$ (Gen2) electrode at different states of charge. The broad resonance at 580 ppm decreased in intensity in the early stages of charging, and a new resonance at 313 ppm appeared and gradually shifted to lower frequencies as the charging proceeded. This suggests that the oxidation of Ni^{3+} to Ni^{4+} occurs first, resulting in an environment containing less Ni^{3+} and therefore decreased hyperfine shift. However, no noticeable change was observed for the resonance at 0 ppm, which was assigned to Li cations in the diamagnetic environment (near to Co).

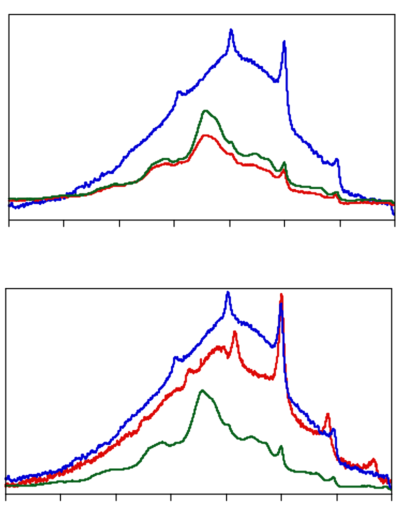


Figure 1. ^{7}Li MAS NMR spectra of $Li_y[Al_{0.11}Mn_{0.89}]O_2$ with O2-type structure.

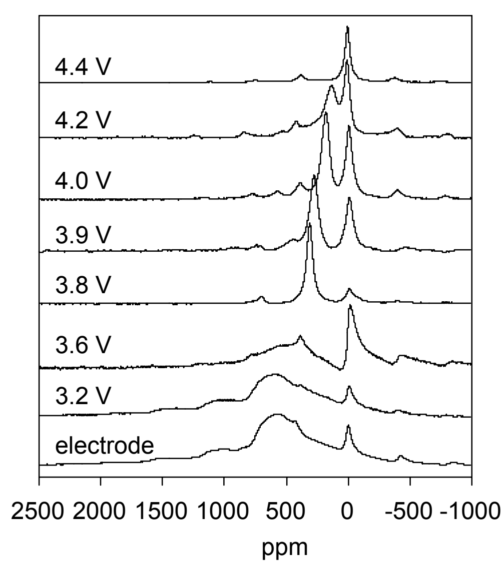


Figure 2. ^{7}Li MAS NMR spectra of $LiAl_{0.05}Ni_{0.80}Co_{0.15}O_2$ (Gen2 cathode).

- **Further plans to meet or exceed milestones:**

• Milestones 1 and 3 above have been completed on schedule for the Mn spinel and the doped Mn spinels. We are performing similar work on the layered Mn oxides and the $LiFePO_4$ –based materials. New milestones will be set for these parts of the work. Milestone 2 was completed on schedule. The results were reported and are being published
• We will continue to obtain NMR spectra of the layered $Li_y[Al_{0.11}Mn_{0.89}]O_2$ with O2-type structure at various temperatures and various states of charge using a higher speed MAS probe. This information will aid in optimizing the composition and understanding the cycling behavior.
• ^{7}Li MAS NMR spectra of $LiFePO_4$ and $Li[Fe,Mn]PO_4$ during charging will be obtained to elucidate the deintercalation mechanism and electrochemical properties.

BATT TASK 6
MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Poor polymer transport properties, side reactions, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use simulations and experiments to explore role of SEI layer in capacity fade in alloy and insertion electrodes. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2001: Measurements of the transport properties of PEMO-LiTFSI and refinement of both the galvanostatic polarization method and the transition-time verification method are completed. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes, such as $LiPF_6$ in EC:PC, is ongoing. Measurements of the entropy of reaction in BATT baseline electrode materials are completed. Modeling of the SEI layer is ongoing. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Refinement of a model of dendrite growth to include mechanical stress and surface tension is ongoing, as is experimental work to observe dendrite growth and electrolyte concentration profiles using confocal Raman spectroscopy.

EXPECTED STATUS SEPT. 30, 2002: Analysis of the effect of side reactions on measurements of transport properties will be completed. Molecular dynamics simulations of diffusion coefficients will be completed. Modeling of the SEI layer will be ongoing. Inclusion of mechanical properties in the model of dendrite growth will be completed, and further refinements to the model will be ongoing. *In situ* confocal Raman spectroscopy measurements of dendrite growth and concentration profiles will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:
1. Model of the effect of side reactions on transport property measurements. Completed.
2. Molecular dynamics simulation of $LiPF_6$ in carbonate solvents. Completed.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** Completed (see previous quarterly report).

- **Accomplishments toward milestone 2 during last quarter:** Completed. Diffusion coefficients calculated using the molecular-dynamics simulation are in qualitative agreement with experimental values for $LiPF_6$ in propylene carbonate and dimethyl carbonate/ethyl-methyl carbonate mixtures. The results indicate that conductivity decreases and viscosity increases as salt concentration increases because of strong ion-association which leads to chain-like structures of relatively immobile ions. The results also indicate that solvent separation in multicomponent electrolytes due to different degrees of dragging of different carbonate solvents by the ions will be negligible. A new computational algorithm for computing long-range atomic interactions in the simulation was developed which reduces computation time by 10%. This algorithm has broad applicability for molecular-dynamics simulations in other fields such as biology.

<u>Other Progress</u>

Work on the model of dendrite growth is ongoing. Previous work showed that prevention of dendrite initiation is necessary, because any dendrite initiated will eventually wreak havoc. The goal of this effort is then to identify if there exist materials properties which could suppress dendrite initiation. In order to treat arbitrarily-shaped and –spaced surface roughness, a general solution to the equations of linear elasticity in 3-D with arbitrarily-shaped boundaries has been obtained. Preliminary experimental data show that the polymer electrolytes of interest behave elastically; therefore, the modeling effort is now focusing on elastic rather than viscoelastic separators. Because of difficulties in maintaining optically transparent, airtight cells uniformly at 85˚C within the confocal Raman microscope, the experiments to measure transport properties of polymers at elevated temperatures have been cancelled.

Refinements to the model of ion and electron transport through the SEI layer are ongoing.

dualfoil.f is a computer program that simulates the behavior of lithium and lithium-ion cells. Written in 1993 by Doyle, Fuller, and Newman and available on our website at ww.cchem.berkeley.edu/jsngrp/fortran.html, it has been used by battery companies and researchers around the world to optimize lithium-battery performance. A users' manual has been added to the website in response to the frequent questions we receive about this program.

A model of iron phosphate electrodes has been completed which describes the diffusion of lithium in the solid phase and the phase change in the material using a shrinking core approach, variable diffusion coefficient, and two particle sizes. Comparison to experimental data (obtained from Kathy Striebel) is in progress to identify which factors limit accessible capacity at high current densities.

In May 2002 a second post-doctoral researcher joined the group. Work has been initiated in conjunction with Tom Richardson to develop novel methods for overcharge protection. A preliminary model of an electronically conducting polymer for overcharge protection has been developed to describe the how the change from insulator to conductor upon oxidation affects the current-voltage behavior of the polymer electrode. Future work will compare the model to experiments in order to measure kinetic parameters and electronic conductivity as functions of degree of oxidation of the polymer.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2000: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2001: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by ANL, by May 31, 2002 (start date: 2/01).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter: We have now completed all measurements of anode conductivity of materials provided by LBNL (Dr. Kathryn Striebel). From the LBNL materials, the anode electrodes of the four sets, i.e. low-cost baseline, GDR, SL-25, and Qu To summarize our efforts, we have continued work in two areas:

1. Experimental conductivity mapping of anode materials provided by three DOE-sponsored laboratories, has been completed, using a sensitive four-probe conduction experiment.
2. Experimental conductivity mapping of cathode materials provided by three DOE-sponsored laboratories, has been initiated, using the four-probe conduction method.

From the LBNL materials, the anode electrodes of the four sets, i.e. low-cost baseline, GDR, SL-25, and Quallion anode, were tested. Anode compression appears to affect the conductivity of electrodes, differently. Specifically,

- for thinner anodes, compression has little effect in reducing resistivity,
- for thicker anodes, compression increased conductivities, overall, and
- contact resistance was higher in compressed anodes.

SEM imaging of the electrodes on edge revealed significant variability in the quality of the interface between active material and current collector (Figure 1); we will determine any statistically significant correlations in the interface quality and resistance in the next quarter.

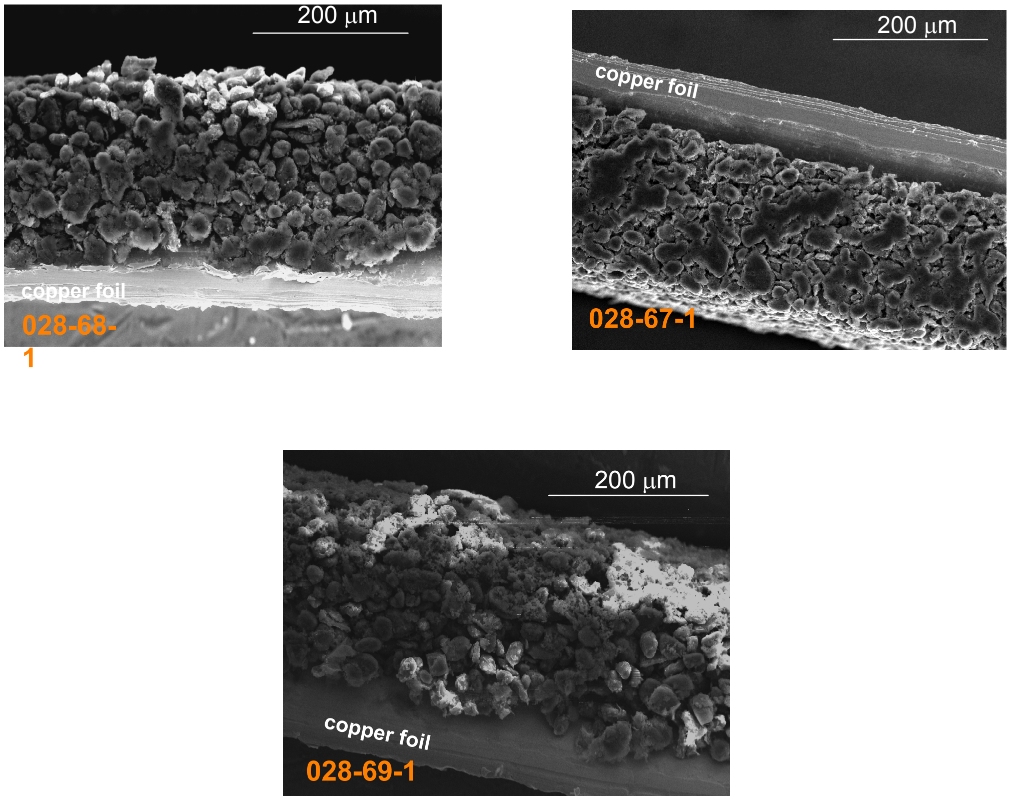


Figure 1. Sample SEM images for anodes.

Electrode	active material		binder		pressing
	name	wt%	name	wt%	
028-67-1	SL20	90	PvdF	10	no
028-68-1	GDR6	90	PvdF	10	no
028-69-1	GDR14	90	PvdF	10	no

Table 1. Compositions of the anodes studied.

- **Further plans to meet or exceed milestones:** We are continuing to test LBNL materials, per continued discussions with Dr. Striebel and Dr. Frank McLarnon. We are now analyzing our results to determine relationships among conduction, composition, and manufacturing conditions. Reduction of data is being automated to accomplish this.

- **PROPOSALS UNDER REVIEW**

ORGANIZATION *(Principal Investigator)*	**TITLE**	**STATUS**
University of Texas at Austin *(J.B. Goodenough)*	Cathodes - Novel Materials	Unsolicited - Contract Placed
Massachusetts Inst. of Tech. *(G. Ceder)* SUNY @ Stony Brook *(C. Grey)*	High Capacity, Stable Cathode Materials in Lithium and Lithium-Ion Batteries	Unsolicited - Contract Placed

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT FOR APRIL – SEPTEMBER 2002

CALENDAR OF UPCOMING EVENTS

<u>May 2002</u>

12 - 17	201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)
19 - 24	8th International Symposium on Polymer Electrolytes –Santa Fe, NM (Rose Romero, ISPE8 Materials Science and Technology Division, Los Alamos National Laboratory, MS G754, P. O. Box 1663, Los Alamos, NM 87545, USA; http://www.lanl.gov/ispe8)

<u>June 2002</u>

23 – 28	11th International Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB 11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/011/imlb11.html)

<u>July 2002</u>

14 – 19	EESAT 2002 - International Ceramics Congress - Materials for Electrochemical, Chemical, Nuclear and Environmental Applications – Florence Italy (Dr. Nancy Clark, Sandia National Laboratories, P.O. Box 5800, MS 0613, Albuquerque NM 87185; nhclark@sandia.gov; http://www.dinamica.it/cimtec)

<u>September 2002</u>

3 - 8	53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut fur Physikalische Chemie II, Universitat Dusseldorf, Universitatsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49 2118112803; schultzj@rz.uni-duesseldorf.de)

<u>October 2002</u>

15 - 18	17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; electricevent17@aol.com).
6 - 11	202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

<u>June 2003</u>

1 - 6	1st International Conference on Polymer Batteries and Fuel Cells (PBFC-1) – Jeju Island, Korea (PBFC-1 Conference Chairman, Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejon, 305-701, KOREA; http://pbfc.kaise.ac.kr)
22 - 27	4th Iinternational Solid State Ionics Meeting - Monterey, CA (Turgut Gur, Stanford University, turgut@stanford.edu), Asilomar

<u>August 2003</u>

31 – Sept. 5	54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

<u>September 2004</u>

	55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)